

Appendix A

**EXAMPLE NAICS AND SIC CODES FOR THE
METAL PRODUCTS & MACHINERY FINAL
EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS**

Appendix A

Example NAICS and SIC codes for the Metal Products & Machinery Final Effluent Limitations Guidelines and Standards

The scope of the MP&M regulation includes facilities that discharge process wastewater from oily operations and manufacture, maintain, or rebuild metal parts, products, or machines used in the following sectors: Aerospace, Aircraft, Bus & Truck, Electronic Equipment, Hardware, Household Equipment, Instruments, Mobile Industrial Equipment, Motor Vehicles, Office Machines, Ordnance, Precious Metals and Jewelry, Railroad, Ships and Boats, Stationary Industrial Equipment, and Miscellaneous Metal Products. In addition, state, local and federal government facilities that discharge wastewater from oily operations and manufacture, maintain, or rebuild metal parts, products or machines (e.g., a town that operates its own bus, truck, and/or snow removal equipment maintenance facility) are also covered by the MP&M rule.

EPA also evaluated job shops and printed wiring board facilities for the final rule (see Section 6.0). As described in Section 9.0, these facilities are not regulated by the MP&M effluent guidelines.

Table A-1 lists of example Standard Industrial Classification (SIC) codes and North American Industrial Classification System (NAICS) codes associated with the various MP&M industrial sectors and the two industrial sectors also reviewed for the final rule. Please note that this list is not intended to be exhaustive, but rather it provides a guide regarding entities that may be within the scope of the MP&M industry.

Table A-1

Example SIC and NAICS Codes Associated with MP&M Industrial Sectors

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|---|----------|---|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Aerospace</i> | | |
| 33641400 | 3761 | Guided Missiles and Space Vehicles |
| 33641500 | 3764 | Guided Missile and Space Vehicle Propulsion |
| 33641900 | 3769 | Other Space Vehicle and Missile Parts |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|---|----------|--|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Aircraft</i> | | |
| 33641100 | 3721 | Aircraft |
| 33641200 | 3724 | Aircraft Engines and Engine Parts |
| 33641300 33291220 33399520 33399620 | 3728 | Aircraft Parts and Auxiliary Equipment |
| 48811110 48811910 48819000 56172020 | 4581 | Airports, Flying Fields, Airport Terminal Services |
| <i>Bus And Truck</i> | | |
| 33621120 | 3713 | Truck and Bus Bodies |
| 33621200 | 3715 | Truck Trailers |
| 48511100 48511200 48511300 48511900 | 4111 | Local and Suburban Transit |
| 48532000 48541020 48599100 48599920 62191090 | 4119 | Local Passenger Transit, N.E.C. |
| 48521000 | 4131 | Intercity and Rural Bus Transportation |
| 48551010 | 4141 | Local Bus Charter Service |
| 48551020 | 4142 | Bus Charter Service, Except Local |
| 48849010 | 4173 | Bus Terminal and Service Facilities |
| 48411010 48411020 | 4212 | Local Trucking without Storage |
| 48412100 48412200 48421020 | 4213 | Trucking, Except Local |
| 48411030 48411040 | 4214 | Local Trucking with Storage |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|--|-----------------|---|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Bus and Truck (Continued)</i> | | |
| 49211010 49221000 | 4215 | Courier Services, Except by Air |
| 48849020 | 4231 | Trucking Terminal Facilities |
| <i>Electronic Equipment</i> | | |
| 33421000 | 3661 | Telephone and Telegraph Apparatus |
| 33422010 | 3663 | Radio and Television Broadcast and Communications Equipment |
| 33429000 | 3669 | Communications Equipment, N.E.C. |
| 33441100 | 3671 | Electron Tubes |
| 33441400 | 3675 | Electronic Capacitors |
| 33441610 33441620 | 3677 | Electronic Coils and Transformers |
| 33441700 | 3678 | Connectors for Electronic Applications |
| 33422020 33441820 33441900 33632210 | 3679 | Electronic Components, N.E.C. |
| 33451010 33451110 33451610 33451910 33512920 33599920 33911410 | 3699 | Electrical Machinery, Equipment, and Supplies, N.E.C. |
| <i>Hardware</i> | | |
| 32312220 | 2796 | Platemaking and Related Services |
| 33281100 | 3398 | Metal Heat Treating |
| 33243910 | 3412 | Metal Shipping Barrels, Drums, Kegs, Pails |
| 33221110 | 3421 | Cutlery |
| 33221210 33221240 | 3423 | Hand and Edge Tools, Except Machine Tools and Handsaws |
| 33221300 | 3425 | Hand Saws and Saw Blades |
| 33243920 | 3429 | Hardware, N.E.C. |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|---|----------|---|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Hardware (Continued)</i> | | |
| 33341410 | 3433 | Heating Equipment, Except Electric and Warm Air Furnace |
| 33231210 | 3441 | Fabricated Structural Metal |
| 33231300 | 3443 | Fabricated Plate Work (Boiler Shops) |
| 33243930 | 3444 | Sheet Metal Work |
| 33232310 | 3446 | Architectural and Ornamental Metal Work |
| 33231100 | 3448 | Prefabricated Metal Buildings and Components |
| 33231220 | 3449 | Miscellaneous Metal Work |
| 33272100 | 3451 | Screw Machine Products |
| 33272200 | 3452 | Bolts, Nuts, Screws, Rivets, and Washers |
| 33211100 | 3462 | Iron and Steel Forgings |
| 33211500 | 3466 | Crowns and Closures |
| 33221400 | 3469 | Metal Stamping, N.E.C. |
| 33291210 | 3492 | Fluid Power Valves and Hose Fittings |
| 33261100 | 3493 | Steel Springs |
| 33291920 | 3494 | Valves and Pipe Fittings, Except Brass |
| 33451810 | 3495 | Wire Springs |
| 33261830 | 3496 | Miscellaneous Fabricated Wire Products |
| 33299620 | 3498 | Fabricated Pipe and Fabricated Pipe Fitting |
| 33243940 33251020 33211700 33721540 33991420 | 3499 | Fabricated Metal Products, N.E.C. |
| 33351210 | 3541 | Machine Tools, Metal Cutting Types |
| 33351300 | 3542 | Machine Tools, Metal Forming Types |
| 33351400 | 3544 | Special Dies and Tools, Die Sets, Jigs and Fixtures, and Industrial Molds |
| 33351500 | 3545 | Machine Tool Access and Measuring Devices |
| 33399100 | 3546 | Power Driven Hand Tools |
| 33999320 | 3965 | Fasteners, Buttons, Needles, Pins |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|---|----------|---|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Household Equipment</i> | | |
| 33712400 | 2514 | Metal Household Furniture |
| 33721400 | 2522 | Office Furniture, Except Wood |
| 33712710 | 2531 | Public Building and Related Furniture |
| 33721530 | 2542 | Partitions and Fixtures, Except Wood |
| 33792000 | 2591 | Drapery Hardware and Window Blinds/shades |
| 33712720 33911310 | 2599 | Furniture and Fixtures, N.E.C. |
| 33299800 | 3431 | Metal Sanitary Ware |
| 33291300 | 3432 | Plumbing Fittings and Brass Goods |
| 33232120 | 3442 | Metal Doors, Sash, and Trim |
| 33522100 | 3631 | Household Cooking Equipment |
| 33522200 | 3632 | Household Refrigerators and Home and Farm and Freezers |
| 33522400 | 3633 | Household Laundry Equipment |
| 33521100 33341420 | 3634 | Electric Housewares and Fans |
| 33521210 | 3635 | Household Vacuum Cleaners |
| 33521220 33522800 | 3639 | Household Appliances, N.E.C. |
| 33511000 | 3641 | Electric Lamps |
| 33593100 | 3643 | Current-Carrying Wiring Devices |
| 33593200 | 3644 | Noncurrent-Carrying Wiring Devices |
| 33512120 | 3645 | Residential Electrical Lighting Fixtures |
| 33512200 | 3646 | Commercial, Industrial, and Institutional |
| 33512910 | 3648 | Lighting Equipment, NEC |
| 33431000 | 3651 | Radio/Television Sets Except Communication Types |
| 81131030 81141220 | 7623 | Refrigeration and Air-conditioning Service and Repair Shops |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|---|----------|---|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Instruments</i> | | |
| 33451120 | 3812 | Search, Detection, Navigation, Guidance, Aeronautical, Nautical Systems and Instruments |
| 33911100 | 3821 | Laboratory Apparatus and Furniture |
| 33451200 | 3822 | Automatic Environmental Controls |
| 33451300 | 3823 | Process Control Instruments |
| 33451400 | 3824 | Fluid Meters and Counting Devices |
| 33451500 | 3825 | Instruments to Measure Electricity |
| 33451620 | 3826 | Laboratory Analytical Instruments |
| 33331420 | 3827 | Optical Instruments and Lenses |
| 33451920 | 3829 | Measuring and Controlling Devices, N.E.C. |
| 33911210 33911220 | 3841 | Surgical and Medical Instruments and Apparatus |
| 32229120 33451020 33911320 | 3842 | Orthopedic, Prosthetic and Surgical Supplies |
| 33911420 | 3843 | Dental Equipment and Supplies |
| 33451700 | 3844 | X-ray Apparatus and Tubes |
| 33451030 | 3845 | Electromedical Equipment |
| 33911500 | 3851 | Ophthalmic Goods |
| 81121210 81121310 81121910 81141120 81141210 | 7629 | Electric Repair Shop |
| <i>Job Shops^a</i> | | |
| 33281300 | 3471 | Plating and Polishing |
| 33281200 33991210 33991410 | 3479 | Metal Coating and Allied Services |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|--|-----------------|--|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Mobile Industrial Equipment</i> | | |
| 33221220 33311100 33392210 | 3523 | Farm Machinery and Equipment |
| 33221230 33311200 | 3524 | Garden Tractors and Lawn and Garden Equipment |
| 33312000 33392310 33651010 | 3531 | Construction Machinery and Equipment |
| 33313100 | 3532 | Mining Machinery and Equipment, Except Oil Field |
| 33392320 | 3536 | Hoists, Industrial Cranes and Monorails |
| 33243950 33299960 33392400 | 3537 | Industrial Trucks, Tractors, Trailers |
| 33699220 | 3795 | Tanks and Tank Components |
| <i>Motor Vehicle</i> | | |
| 33637000 | 3465 | Automotive Stampings |
| 33631100 | 3592 | Carburetors, Piston Rings, Valves |
| 33632100 | 3647 | Vehicular Lighting Equipment |
| 33632220 | 3694 | Electrical Equipment for Motor Vehicles |
| 33611100 33611200 33612000 33621110 33621130 33699210 | 3711 | Motor Vehicle and Automobile Bodies |
| 33621130 | 3714 | Motor Vehicle Parts and Accessories |
| 33621300 | 3716 | Mobile Homes |
| 33699110 | 3751 | Motorcycles |
| 33621410 | 3792 | Travel Trailers and Campers |
| 33699900 | 3799 | Miscellaneous Transportation Equipment |
| 48531000 | 4121 | Taxicabs |
| 44131030 | 5013 | Motor Vehicle Supplies and New Parts |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|---|----------|---|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Motor Vehicle (Continued)</i> | | |
| 44111000 | 5511 | Motor Vehicle Dealers (New and Used) |
| 44112000 | 5521 | Motor Vehicle Dealers (Used Only) |
| 44121000 | 5561 | Recreational Vehicle Dealers |
| 44122100 | 5571 | Motorcycle Dealers |
| 44122900 | 5599 | Automotive Dealers, N.E.C. |
| 53211200 | 7515 | Passenger Car Lease |
| 81112110 81112120 81112130 | 7532 | Top, Body, and Upholstery Repair and Paint Shops |
| 81111200 | 7533 | Auto Exhaust Systems |
| 81111300 | 7537 | Auto Transmission Repair |
| 81111100 | 7538 | General Automotive Repair |
| 81111810 81111820 81111830 81111840 81111890 | 7539 | Auto Repair Shop, N.E.C. |
| 81119100 81119820 | 7549 | Auto Services, Except Repair and Carwashes |
| <i>Office Machines</i> | | |
| 33411100 | 3571 | Electronic Computers |
| 33411200 | 3572 | Typewriters |
| 33411300 | 3575 | Computer Terminals |
| 33411910 | 3577 | Computer Peripheral Equipment, N.E.C. |
| 33411920 | 3578 | Calculating, Accounting Machines Except Computers |
| 33451820 | 3579 | Office Machines, N.E.C. |
| 81121230 | 7378 | Computer Maintenance and Repairs |
| 54151220 54151910 33451820 | 7379 | Computer Related Services, N.E.C. |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|--|-----------------|--|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Ordnance</i> | | |
| 33299200 | 3482 | Small Arms Ammunition |
| 33299300 | 3483 | Ammunition, Except for Small Arms |
| 33299400 | 3484 | Small Arms |
| 33299500 | 3489 | Ordnance and Accessories, N.E.C. |
| <i>Precious Metals and Jewelry</i> | | |
| 33451830 | 3873 | Watches, Clocks, and Watchcases |
| 33991120 | 3911 | Jewelry, Precious Metal |
| 33991220 | 3914 | Silverware, Plated Ware and Stainless |
| 33991300 | 3915 | Jewelers' Materials and Lapidary Work |
| 33991430 | 3961 | Costume Jewelry |
| 81149010 | 7631 | Watch, Clock, Jewelry Repair |
| <i>Printed Circuit Boards^a</i> | | |
| 33441200 | 3672 | Printed Circuit Boards |
| <i>Railroad</i> | | |
| 33391120 33651020 | 3743 | Railcars, Railway Systems |
| 48211100 | 4011 | Railroad Transportation |
| 48211200 | 4013 | Railroad Transportation |
| <i>Ships and Boats</i> | | |
| 33661100 | 3731 | Ship Building and Repairing |
| 33661200 81149020 | 3732 | Boat Building and Repairing |
| 48311100 | 4412 | Deep Sea Foreign Transportation |
| 48311310 | 4424 | Deep Sea Domestic Transportation |
| 48311320 | 4432 | Freight Transportation Great Lakes |
| 48321110 | 4449 | Water Transportation of Freight, N.E.C. |
| 48311410 | 4481 | Deep Sea Passenger Transportation |
| 48311420 | 4482 | Ferries |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|---|----------|--|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Ships and Boats (Continued)</i> | | |
| 48321220 48721010 | 4489 | Water Passenger Transportation, N.E.C. |
| 48831010 | 4491 | Marine Cargo Handling |
| 48321120 | 4492 | Towing and Tugboat Service |
| 71393000 | 4493 | Marinas |
| 48831020 48833020 48833030 48839010 53241110 | 4499 | Water Transportation Services, N.E.C. |
| <i>Stationary Industrial Equipment</i> | | |
| 33361100 | 3511 | Steam, Gas, Hydraulic Turbines, Generating Units |
| 33639910 | 3519 | Internal Combustion Engines, N.E.C. |
| 33313200 | 3533 | Oil Field Machinery and Equipment |
| 33392100 | 3534 | Elevators and Moving Stairways |
| 33392220 | 3535 | Conveyors and Conveying Equipment |
| 33299700 | 3543 | Industrial Patterns |
| 33351600 | 3547 | Rolling Mill Machinery and Equipment |
| 33399210 | 3548 | Electric and Gas Welding and Soldering |
| 33351800 | 3549 | Metal Working Machinery, N.E.C. |
| 33329210 | 3552 | Textile Machinery |
| 33321000 | 3553 | Woodworking Machinery |
| 33329100 | 3554 | Paper Industries Machinery |
| 33329310 | 3555 | Printing Trades Machinery and Equipment |
| 33329400 | 3556 | Food Products Machinery |
| 33329810 | 3559 | Special Industry Machinery, N.E.C. |
| 33391110 | 3561 | Pumps and Pumping Equipment |
| 33299100 | 3562 | Ball and Roller Bearings |
| 33391200 | 3563 | Air and Gas Compressors |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|--|----------|---|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Stationary Industrial Equipment (Continued)</i> | | |
| 33341200 33341100 | 3564 | Blowers and Exhaust and Ventilation Fans |
| 33399300 | 3565 | Industrial Patterns |
| 33361200 | 3566 | Speed Changers, High Speed Drivers and Gears |
| 33399400 | 3567 | Industrial Process Furnaces and Ovens |
| 33361300 | 3568 | Mechanical Power Transmission Equipment, N.E.C. |
| 33399910 | 3569 | General Industrial Machinery, N.E.C. |
| 33331100 | 3581 | Automatic Merchandising Machines |
| 33331200 | 3582 | Commercial Laundry Equipment |
| 33639100 | 3585 | Refrigeration and Air and Heating Equipment |
| 33391300 | 3586 | Measuring and Dispensing Pumps |
| 33331920 | 3589 | Service Industry Machines, N.E.C. |
| 33399510 | 3593 | Fluid Power Cylinders and Actuators |
| 33399610 | 3594 | Fluid Power Pumps and Motors |
| 33399700 | 3596 | Scales and Balances, Except Laboratory |
| 33399920 | 3599 | Machinery, Except Electrical, N.E.C. |
| 33531120 | 3612 | Transformers |
| 33531300 | 3613 | Switchgear and Switchboard Apparatus |
| 33531210 | 3621 | Motors and Generators |
| 33599910 | 3629 | Electric Industrial Apparatus, N.E.C. |
| 53241210 | 7353 | Heavy Construction Equipment Rental, Leasing |
| 53221000 53229990 53231000 53241190 53241290 53242010 53249020 56299120 | 7359 | Equipment Rental, Leasing, N.E.C. |

Table A-1 (Continued)

| Example NAICS and SIC Codes for the MP&M Industrial Sectors | | |
|--|----------|---|
| NAICS Code | SIC Code | Standard Industrial Classification Groups |
| <i>Miscellaneous Metal Products</i> | | |
| 33299940 | 3497 | Metal Foil and Leaf |
| 33331520 | 3861 | Photographic Equipment and Supplies |
| 33999200 | 3931 | Musical Instruments |
| 33699120 | 3944 | Games, Toys, Children's Vehicles |
| 33992000 | 3949 | Sporting and Athletic Goods, N.E.C. |
| 33994100 | 3951 | Pens and Mechanical Pencils |
| 33994300 | 3953 | Marking Devices |
| 33995000 | 3993 | Signs and Advertising Displays |
| 33999500 | 3995 | Burial Caskets |
| 33221270 33299980 33512130 | 3999 | Manufacturing Industries, N.E.C. |
| 81149030 | 7692 | Welding Repair |
| 48839030 81149090 56162200 56179010 81121220 81121990 81131010 81141110 81141290 | 7699 | Repair Shop, Related Service |
| <i>Continuous Electroplaters</i> | | |
| 33281300 | 3399 | Electroplating, Plating, Polishing, Anodizing, and Coloring |

Source: U.S. Census Bureau, North American Industrial Classification System,
<http://www.census.gov/epcd/www/naics.html>.

N.E.C. - Not elsewhere classified.

^aIndustrial sector considered, but not included, in Part 438.

Appendix B

ANALYTICAL METHODS AND BASELINE VALUES FOR THE METAL PRODUCTS AND MACHINERY INDUSTRY

APPENDIX B

ANALYTICAL METHODS AND BASELINE VALUES

- B.1 Nominal Quantitation Limits
- B.2 Baseline Values
- B.3 Analytical Results Reporting Conventions
- B.4 Analytical Methods
 - B.4.1 EPA Methods 1624, 1625, 1664, and OIA-1677 (Volatile Organics, Semivolatile Organics, SGT-HEM, HEM, and Available Cyanide)
 - B.4.2 EPA Methods 1620 and 200.7 (Metals)
 - B.4.3 EPA Method 335.1 (Amenable Cyanide)
 - B.4.4 EPA Methods 350.2 and 350.3 (Ammonia as Nitrogen)
 - B.4.5 EPA Method 405.1 and SM 5210B (BOD₅ and Carbonaceous BOD)
 - B.4.6 EPA Methods 410.1, 410.2, and 410.4 (Chemical Oxygen Demand)
 - B.4.7 EPA Method 325.3 (Chloride)
 - B.4.8 EPA Method 340.2 (Fluoride)
 - B.4.9 EPA Method 218.4, SM 3111A, and SM 3500D (Hexavalent Chromium)
 - B.4.10 EPA Method 150.1 and SM 4500H (pH)
 - B.4.11 EPA Methods 375.2 and 375.4 (Sulfate)
 - B.4.12 EPA Methods 335.2 and 335.3 (Total Cyanide)
 - B.4.13 EPA Method 160.1 and SM 2540C (Total Dissolved Solids)
 - B.4.14 EPA Method 351.3 (Total Kjeldahl Nitrogen)
 - B.4.15 EPA Method 415.1 (Total Organic Carbon)
 - B.4.16 EPA Methods 420.1 and 420.2 (Total Phenols)
 - B.4.17 EPA Methods 365.2 and 365.3 (Total Phosphorus)
 - B.4.18 EPA Methods 376.1 and 376.2, SM 4500D and SM 4500E, and D4658 (Total Sulfide)
 - B.4.19 EPA Method 160.2 and SM 2540D (Total Suspended Solids)
 - B.4.20 EPA Methods 204.1 and 7041 (Antimony)
 - B.4.21 EPA Methods 206.2 and 7060A (Arsenic)
 - B.4.22 EPA Method 231.2 (Gold)
 - B.4.23 EPA Method 239.1 (Lead)
 - B.4.24 EPA Methods 245.1 and 245.2 (Mercury)
 - B.4.25 EPA Method 265.2 (Rhodium)
 - B.4.26 EPA Methods 270.2 and 7740 (Selenium)
 - B.4.27 EPA Method 272.1 (Silver)
 - B.4.28 EPA Methods 279.1 and 7841 (Thallium)
 - B.4.29 EPA Methods 624 and 625 (Volatile Organics and Semivolatile Organics)
 - B.4.30 EPA Method 630.1 (Ziram)
- B.5 Analytical Method Development Efforts

The analytical methods described in this appendix were used to determine pollutant levels in wastewater samples collected by EPA and industry at a number of metal products and machinery facilities. (Sampling efforts are described in Section 3.0) In developing the rule, EPA used data from samples collected by EPA and industry to determine the levels of amenable cyanide, ammonia as nitrogen, available cyanide, biochemical oxygen demand (BOD), carbonaceous biochemical oxygen demand, chemical oxygen demand (COD), chloride, fluoride, hexavalent chromium, metals, oil and grease (measured as hexane extractable material (HEM)), pH, semivolatile organics, silica gel-treated hexane extractable material (SGT-HEM), sulfate, total cyanide, total dissolved solids (TDS), total Kjeldahl nitrogen (TKN), total organic carbon (TOC), total phenols, total phosphorus, total sulfide, total suspended solids (TSS), volatile organics, and ziram. As explained in Section 7.0, EPA is regulating a subset of these pollutants.

Sections B.1 and B.2 of this appendix provide explanations of nominal quantitation limits and baseline values. Section B.3 describes the reporting conventions used by laboratories in expressing the results of the analyses. Section B.4 describes each analytical method and the corresponding baseline values that EPA used in determining the pollutants of concern. Section B.5 discusses analytical method development efforts. Table B-1 identifies the analytical methods and baseline values for each pollutant, identifies each pollutant by Chemical Abstract Service Registry Number, indicates whether the samples were collected by EPA and/or by industry, and lists the nominal quantitation value for the method used.

B.1 Nominal Quantitation Limits

The nominal quantitation limit is the smallest quantity of an analyte that can be reliably measured with a particular method, using the typical (nominal) sample size. The protocols used for determination of nominal quantitation limits in a particular method depend on the definitions and conventions that EPA used at the time the method was developed. The nominal quantitation limits associated with the methods addressed in this section fall into three categories.

- 1) The first category pertains to EPA Methods 1624, 1625, 1664, and OIA-1677, which define the minimum level (ML) as the lowest level at which the entire analytical system must give a recognizable signal and an acceptable calibration point for the analyte. These methods are described in Section B.4.1.
- 2) The second category pertains specifically to EPA Method 1620, and is explained in detail in Section B.4.2.
- 3) The third category pertains to the remainder of the chemical methods in which a variety of terms are used to describe the lowest level at which measurement results are quantitated. In some cases (especially with the classical wet chemistry analytes) the methods date to the 1970s and 1980s when different concepts of quantitation were employed by EPA. These methods typically list a measurement range or lower limit of

measurement. The terms differ by method and, as discussed in subsequent sections, the levels presented are not always representative of the lowest levels laboratories currently can achieve.

For those methods associated with a calibration procedure, the laboratories demonstrated through a low-point calibration standard that they were capable of reliable quantitation at method-specified (or lower) levels. In such cases these nominal quantitation limits are operationally equivalent to the ML (though not specifically identified as such in the methods).

In the case of titrimetric or gravimetric methods, the laboratory adhered to the established lower limit of the measurement range published in the methods. Details of the specific methods are presented in Sections B.4.3 through B.4.30.

B.2 Baseline Values

As described further in Section 7.0, in determining the pollutants of concern, EPA compared the reported concentrations for each pollutant to a multiple of the baseline value. As described in Section B.3 and shown in Table B-1, for most pollutants, the baseline value was set equal to the nominal quantitation limit for the analytical method. EPA made two general types of exceptions which are briefly described below. Section B.4 provides additional details about these exceptions in the context of the analytical methods.

The first type of exception was for baseline values that were different than the nominal quantitation limits in the analytical methods. When the baseline values were lower, EPA made these exceptions because the laboratory submitted data that demonstrated that reliable measurements could be obtained at lower levels for those pollutants. When the baseline values were higher, EPA concluded that the nominal quantitation limit for a specified method was less than the level that laboratories could reliably achieve and adjusted the baseline value upward.

The second type of exception was for baseline values set at a common value for multiple analytical methods for the same pollutant. For some analytes, EPA permitted the laboratories to choose between methods to accommodate sample characteristics and/or industry used a different analytical method than EPA. When these methods had different nominal quantitation limits, EPA generally used the one with the lowest value or the one associated with the method used for most samples.

B.3 Analytical Results Reporting Conventions

The laboratories reported each analytical result either as a numeric value or as not quantitated¹. A numeric result indicates that the pollutant was quantitated² in the sample. Most analytical results were reported as liquid concentrations in weight/volume units (e.g., micrograms per liter ($\mu\text{g/L}$)), except for the pH data, which were reported in "standard units" (SU). For solid samples, the results were provided in weight/weight units (e.g., milligrams per kilogram (mg/kg)). In those instances, EPA converted the solids results into weight/volume units by using a conversion factor based on the percentage of solids in the samples.

For example, the result for a hypothetical pollutant X would be reported as "15 g/L" when the laboratory cannot quantitate the amount of pollutant X in the sample as being 15 g/L. When the laboratory cannot quantitate the amount of pollutant X in the sample, the laboratory would report that the analytical result indicated a value less than the sample-specific quantitation limit of 10 g/L (i.e., "<10 g/L"). The actual amount of pollutant X in that sample is between zero (i.e., the pollutant is not present) and 10 g/L. The sample-specific quantitation limit for a particular pollutant is generally the smallest quantity in the calibration range that can be measured reliably in any given sample. Reporting a pollutant as nonquantitated does not mean that the pollutant is not present in the wastewater; it merely indicates that analytical techniques (whether because of instrument limitations, pollutant interactions, or other reasons) do not permit its measurement at levels below the sample-specific quantitation limit.

In its calculations, EPA generally substituted the reported sample-specific quantitation limit for each nonquantitated result. As described in Section B.4.1, EPA substituted the baseline value for the nonquantitated result when the sample-specific quantitation limit was less than the baseline value. In addition, when the detected quantitated value was below the baseline value, EPA substituted the baseline value for the measured value and considered these values to be nonquantitated in the statistical analyses.

B.4 Analytical Methods

EPA and industry analyzed all metal products and machinery facility wastewater samples using methods identified in Table B-1. (As explained in Section 7.0, EPA is regulating only a subset of these analytes.) In analyzing samples, EPA generally used analytical methods approved at 40 CFR 136 or methods that EPA has used for decades in support of effluent guidelines development. Exceptions for use of nonapproved methods are explained in the method-specific subsections that

¹Elsewhere in this document and in the preamble to the rule, EPA may refer to pollutants as "not detected" or "nondetected." This appendix uses the terms "not quantitated" or "nonquantitated" rather than not detected or nondetected.

²Elsewhere in this document and in the preamble to the rule, EPA may refer to pollutants as "detected." This appendix uses the term "quantitated" rather than detected.

follow. EPA proposed limitations or standards based only upon data generated by methods approved in 40 CFR 136. Table B-1 provides a summary of the analytical methods, the associated pollutants measured by the method, the nominal quantitation levels, and the baseline levels. The following sections provide additional information supporting the summary in Table B-1.

The following sections describe the methods used to determine pollutant levels in wastewater samples collected at metal products and machinery facilities. Each section states whether the method is approved at 40 CFR 136 (even if the pollutant was not proposed to be regulated), provides a short description of the method, identifies the nominal quantitation limit, and explains EPA's choice for the baseline value.

B.4.1 EPA Methods 1624, 1625, 1664, and OIA- 1677 (Volatile Organics, Semivolatile Organics, HEM, SGT-HEM, and Available Cyanide)

EPA used Methods 1624, 1625, 1664, and OIA-1677 to measure volatile organics, semivolatile organics, n-hexane extractable material (HEM)/silica gel treated n-hexane extractable material (SGT- HEM) and available cyanide, respectively. Industry used Method 1664 to measure HEM and SGT-HEM. Methods 1624, 1625, 1664, and OIA-1677 are approved at 40 CFR 136.

These methods use the minimum level (ML) of quantitation. The ML is defined as the lowest level at which the entire analytical system must give a recognizable signal and an acceptable calibration point for the analyte. When an ML is published in a method, the Agency has demonstrated that the ML can be achieved in at least one well-operated laboratory. When that laboratory or another laboratory uses that method, the laboratory is required to demonstrate, through calibration of the instrument or analytical system, that it can achieve pollutant measurements at the ML.

For volatile organics, semivolatile organics, HEM/SGT-HEM, and available cyanide, EPA used the method-specified MLs as the baseline values. In determining the pollutants of concern and in calculating the HEM/SGT-HEM standards, EPA substituted the value of the ML and assumed that the measurement was not quantitated when a quantitated value or sample-specific quantitation limit was reported with a value less than the ML specified in the method. For example, if the ML was 10 g/L and the laboratory reported a quantitated value of 5 g/L, EPA assumed that the concentration was nonquantitated with a sample-specific quantitation limit of 10 g/L. The objective of this comparison was to identify any results for the pollutants reported below the method-defined ML. Results reported below the ML were changed to the ML to ensure that all results used by EPA were reliable. In most cases, the quantitated values and sample-specific quantitation limits were equal to or greater than the baseline values.

B.4.2 EPA Methods 1620 and 200.7 (Metals)

EPA used Method 1620 to measure the concentrations of metals. While Method 1620 is not listed at 40 CFR 136 as an approved method, it represents a consolidation of the analytical

techniques in several 40 CFR 136-approved methods, such as Method 200.7 (inductively coupled plasma atomic emission (ICP) spectroscopy of trace elements) and Method 245.1 (mercury cold vapor atomic absorption (CVAA) spectroscopy). This method was developed specifically for the effluent guidelines program. Method 1620 includes more metal analytes than are listed in the approved methods and contains quality control requirements at least as stringent as the 40 CFR 136-approved methods. Some industry-supplied results for aluminum, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, magnesium, manganese, molybdenum, nickel, sodium, vanadium, and zinc were determined by Method 200.7. Other industry-supplied results for metals were determined by EPA Methods 204.1, 206.2, 231.2, 239.1, 245.1, 245.2, 265.2, 270.2, 272.1, 279.1, 7041, 7060A, 7740, and 7841.

Method 1620 employs the concept of an instrument detection limit (IDL). The IDL is defined as "the smallest signal above background noise that an instrument can detect reliably."³ Data reporting practices for Method 1620 analyses follow conventional metals reporting practices used in other EPA programs, in which values are required to be reported at or above the IDL. In applying Method 1620, IDLs are determined on a quarterly basis by each analytical laboratory and are, therefore, laboratory-specific and time-specific. Although Method 1620 contains MLs, these MLs pre-date EPA's recent refinements of the ML concept described earlier. The MLs associated with Method 1620 are based on a consensus opinion reached between EPA and laboratories during the 1980s regarding levels that could be considered reliable quantitation limits when using Method 1620. These limits do not reflect advances in technology and instrumentation since the 1980s. Consequently, the IDLs, which are more reflective of current analytical capabilities, were used as the lowest values for reporting purposes, with the general understanding that reliable results can be produced at or above the IDL. Although the baseline values were derived from the MLs (or adjusted MLs) in Method 1620, EPA used the laboratory-reported quantitated values and sample-specific quantitation limits, which captured concentrations down to the IDLs, in its data analyses.

In general, EPA used the MLs specified in Method 1620 as the baseline values. However, EPA adjusted the baseline value for lead to 50 : g/L and boron to 100 : g/L. In Method 1620, lead has an ML of 5 : g/L for graphite furnace atomic absorption (GFAA) spectroscopy analysis; EPA determined, however, that it was not necessary for the laboratories to measure down to such low levels, and that lead could be analyzed by inductively coupled plasma atomic emission (ICP) spectroscopy. Consequently, the ML requirement was adjusted to 50 : g/L, the ML for the ICP method. In Method 1620, boron has an ML of 10 : g/L, but laboratory feedback years ago indicated that laboratories could not reliably achieve this low level. As a result, EPA only required laboratories to measure values at 100 : g/L and above. Thus, EPA adjusted the baseline value to 100 : g/L.

³Keith, L.H., W. Crummett, J. Deegan, R.A. Libby, J.K. Taylor, G. Wentler (1983). "Principles of Environmental Analysis," *Analytical Chemistry*, Volume 55, Page 2217.

B.4.3 EPA Method 335.1 (Amenable Cyanide)

Amenable cyanide was measured using Method 335.1, which is approved at 40 CFR 136. Industry also supplied data determined by Method 335.1. Method 335.1 utilizes either a titrimetric or colorimetric procedure to measure amenable cyanide.

Method 335.1 has a lower measurement range limit of 0.02 milligrams per liter (mg/L) for the colorimetric procedure and a lower measurement range limit of 1 mg/L for the titrimetric procedure. The nominal quantitation limit of 0.02 mg/L was used as the baseline for all amenable cyanide results, since it is the lower value of the two.

B.4.4 EPA Methods 350.2 and 350.3 (Ammonia as Nitrogen)

Ammonia, as nitrogen, was measured using Methods 350.2 and 350.3, both of which are approved at 40 CFR 136. Method 350.2 utilizes colorimetric, titrimetric, or electrode procedures to measure ammonia. Method 350.3 uses a potentiometric procedure to measure ammonia.

Method 350.2 has a lower measurement range limit of 0.20 mg/L for the colorimetric and electrode procedures, and a lower measurement range limit of 1.0 mg/L for the titrimetric procedure. Method 350.3 has a lower measurement range limit of 0.03 mg/L for the potentiometric procedure. Rather than use different baseline values for the same pollutant, EPA used 0.03 mg/L as the baseline value from Method 350.3 because it represents the lowest value at which ammonia as nitrogen can be measured reliably.

B.4.5 EPA Method 405.1 and SM 5210B (BOD₅ and Carbonaceous BOD₅)

Biochemical oxygen demand (BOD₅) and carbonaceous BOD₅ (cBOD₅) were measured using Method 405.1 and Standard Method (SM) 5210B, both of which are approved at 40 CFR 136. BOD₅ and cBOD₅ are determined by the same method, except that an organic compound is added to the cBOD₅ test to inhibit nitrogenous oxygen demand. If the sample does not include any nitrogenous demand to inhibit, the results should be comparable for BOD₅ and cBOD₅.

Method 405.1 and SM 5210B are identical and the nominal quantitation limit, which is expressed in the methods as the lower limit of the measurement range at 2 mg/L, is the same for both forms of BOD₅. EPA used this nominal quantitation limit of 2 mg/L as the baseline value in determining the pollutants of concern.

B.4.6 EPA Methods 410.1, 410.2, and 410.4 (Chemical Oxygen Demand)

Chemical Oxygen Demand (COD) was measured using Methods 410.1, 410.2, and 410.4, all of which are approved at 40 CFR 136. Method 410.4 is a colorimetric procedure. Methods 410.1 and 410.2 are titrimetric procedures that follow identical analytical protocols; they

differ only in the range of COD concentration that they are designed to measure. Reagent concentrations and sample volumes are adjusted to accommodate a wide range of sample concentrations, since the dynamic range of the chemistry used to detect COD is somewhat limited. Data from all three of these methods are directly comparable.

Method 410.1 is designed to measure mid-level concentrations (greater than 50 mg/L) of COD and is associated with a nominal quantitation limit of 50 mg/L. Method 410.2 is designed to measure low-level concentrations in the range of 5-50 mg/L. Method 410.4 has a measurement range of 3-900 mg/L for automated procedures and measurement range of 20-900 mg/L for manual procedures. EPA contracts required that laboratories measure down to the lowest quantitation limit possible for whatever method is used. Therefore, if the laboratory analyzes a sample using Method 410.1 and obtains a nonquantitated result, it must reanalyze the sample using Method 410.2. Thus, the quantitation limit reported for nonquantitated was 5 mg/L, unless sample dilutions were required for complex matrices.

For all COD data, EPA used the baseline value of 5 mg/L that is associated with the lower quantitation limit for the titrimetric procedures because most of the data used to determine COD were obtained by the titrimetric procedures (i.e., Methods 410.1 and 410.2).

B.4.7 EPA Method 325.3 (Chloride)

Chloride was measured using Method 325.3, which is approved at 40 CFR 136. Method 325.3 is a titrimetric procedure and measures concentrations greater than 1 mg/L; therefore, EPA used the baseline value of 1 mg/L.

B.4.8 EPA Method 340.2 (Fluoride)

Fluoride was determined by Method 340.2, which is approved at 40 CFR 136. Method 340.2 is a potentiometric procedure that uses a fluoride electrode. The nominal quantitation limit of 0.1 mg/L is expressed in the method as the lower limit of the measurement range. This nominal quantitation limit was used as the baseline value for fluoride.

B.4.9 EPA Method 218.4, SM 3111A, and SM 3500D (Hexavalent Chromium)

For EPA sampling episodes, hexavalent chromium was determined by Method 218.4 and SM 3500D, which are approved at 40 CFR 136. Industry supplied data generated by SM 3111A which is not approved at 40 CFR 136. Method 218.4 utilizes atomic absorption for the determination of hexavalent chromium after chelation and extraction. SM 3500D is a colorimetric procedure using reaction with diphenylcarbazide to produce a color proportional to Cr^{6+} concentration. SM 3111A utilizes flame atomic absorption spectrometry to measure Cr^{6+} or total Cr.

In Method 218.4, SM 3111A, and SM 3500D, the nominal quantitation limit or lower limit of the measurement range is 0.01 mg/L. Because EPA used Methods 218.4 and SM 3500D for analysis, the nominal quantitation limit of 0.01 mg/L was used as the baseline value for all hexavalent chromium results.

B.4.10 EPA Method 150.1 and SM 4500H (pH)

For EPA sampling episodes, pH was determined by Method 150.1. For industry-supplied data, pH was determined by SM 4500H. Both methods are approved at 40 CFR 136. For Method 150.1 and SM 4500H, the pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. There are no nominal quantitation limits for either Method 150.1 or SM 4500H.

B.4.11 EPA Methods 375.2 and 375.4 (Sulfate)

For EPA sampling episodes, sulfate was measured by Methods 375.2 and 375.4. For industry-supplied data, sulfate was measured by Method 375.4. Both of these methods are approved at 40 CFR 136. Method 375.2 is a colorimetric procedure that uses the decrease in color caused by the formation of barium sulfate to measure the sulfate concentration. Method 375.4 measures the turbidity created by the insoluble barium sulfate in solution. A dispersant/buffer is added to the solution to aid in creating uniform suspension of the barium sulfate.

The nominal quantitation limit (also the lower limit of the measurement range) for Method 375.2 is 0.50 mg/L. The nominal quantitation limit (also the lower limit of the measurement range) for Method 375.4 is 1 mg/L. EPA used the baseline value of 1 mg/L that is associated with the higher quantitation limit for all the sulfate data, rather than having multiple baseline values, because most of the sulfate data was determined by Method 375.4.

B.4.12 EPA Methods 335.2 and 335.3 (Total Cyanide)

EPA determined total cyanide using Method 335.2. Industry determined total cyanide by Methods 335.2 and 335.3. Both methods are approved at 40 CFR 136. Method 335.2 uses either titration with silver nitrate, or colorimetry with an organic dye, to measure total cyanide. Method 335.3 uses an automated distillation-colorimetry procedure for continuous flow analytical systems that utilizes UV oxidation to measure total cyanide.

The nominal quantitation limit for Method 335.2, expressed in the method as the lower limit of the measurement range, is 0.02 mg/L. The nominal quantitation limit for Method 335.3, also expressed as the lower limit of the measurement range, is 0.005 mg/L. Because EPA used Method 335.2, the Agency used the nominal quantitation limit of 0.02 mg/L as the baseline value for all total cyanide results.

B.4.13 EPA Method 160.1 and SM 2540C (Total Dissolved Solids)

EPA determined total dissolved solids (TDS) by Method 160.1. Industry determined TDS by SM 2540C. Both methods are approved at 40 CFR 136 under "residue-filterable." Method 160.1 and SM 2540C are gravimetric methods with a lower limit of the measurement range of 10 mg/L; this value is the nominal quantitation limit. The nominal quantitation limit of 10 mg/L is also the baseline value.

B.4.14 EPA Method 351.3 (Total Kjeldahl Nitrogen)

EPA determined total Kjeldahl nitrogen (TKN) by Method 351.3, which is approved at 40 CFR 136. Method 351.3 is a manual colorimetric analysis that has a lower measurement range limit, which is also the nominal quantitation limit, of 1.0 mg/L. The nominal quantitation limit of 1.0 mg/L is also the baseline value.

B.4.15 EPA Method 415.1 (Total Organic Carbon)

EPA determined total organic carbon (TOC) by Method 415.1, which is approved at 40 CFR 136. Method 415.1 is a combustion (or oxidation) method with a lower measurement range limit of 1 mg/L. EPA used this nominal quantitation limit of 1 mg/L as the baseline value.

B.4.16 EPA Methods 420.1 and 420.2 (Total Phenols)

In EPA's database, the terms "total phenols" and "total recoverable phenolics" are used synonymously. The term "total recoverable phenolics" is used in the titles of Methods 420.1 to 420.4. While "total recoverable phenolics" could be considered a more accurate term for what is measured in any of these related methods, both terms refer to an aggregate measure of compounds with a phenol-like or "phenolic" structure. The use of the adjective "recoverable" simply recognizes that there are some compounds that are not measured, as well as other related compounds in this class. Thus, the method reports what can be recovered from the sample under the conditions of the analysis.

The methods for the analysis of total phenols employ the reagent 4-aminoantipyrine (4AAP), which reacts with phenolic compounds to produce a dark red product, an antipyrine dye. The concentration of the phenolic compounds is determined by measuring the absorbance of the sample at a wavelength of 460 to 520 nm, depending on the method. The methods are calibrated using a series of standards containing the single compound phenol. Methods 420.1 and 420.2, the two methods approved at 40 CFR 136, provide several options for sample preparation and analysis, including a preliminary distillation designed to remove interferences, and a chloroform extraction procedure in Method 420.1 that is designed to improve the sensitivity of the method. Both methods also provide information on the concentrations of the calibration standards that may be prepared for a given set of procedural options.

The methods themselves do not contain a required calibration range. Each laboratory can, and does, establish a calibration range based on its use of the method. EPA used a baseline value of 0.05 mg/L because this was the most commonly reported sample-specific detection limit in EPA's sampling episode data (these data included more concentrated samples than effluent).

B.4.17 EPA Methods 365.2 and 365.3 (Total Phosphorus)

EPA determined total phosphorus by Methods 365.2 and 365.3. Both methods are approved at 40 CFR 136. Total phosphorus represents all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure.

The two methods differ only in the preparation of one of the reagents. Method 365.2 specifies the separation of the ammonium molybdate and the antimony potassium tartrate from the ascorbic acid reagent. Method 365.3 allows for combining these reagents into a single solution. Because the chemistry is unaffected, the data are directly comparable.

These methods have the same nominal quantitation limit of 0.01 mg/L. EPA used this value as the baseline value for total phosphorus.

B.4.18 EPA Methods 376.1 and 376.2, SM 4500D and SM 4500E, and D4658 (Total Sulfide)

EPA determined total sulfide by Methods 376.1, 376.2, and SM 4500E, all of which are approved at 40 CFR 136. Industry determined sulfide by SM 4500D and ASTM Method D4658. SM 4500D is approved at 40 CFR 136, while ASTM Method D4658 is not approved at 40 CFR 136. Method 376.1 and SM 4500E utilize an iodine solution to oxidize any sulfide present in the sample. The remaining iodine is then titrated with sodium thiosulfate in the presence of a starch solution. The quantity of iodine added to the sample and the titrant required to neutralize the remaining iodine give the sulfide concentration by calculation. Method 376.2 and SM 4500D use the reaction of the sulfide ion with ferric chloride and dimethyl-*P*-phenylenediamine to produce deeply colored methylene blue. The color is proportional to the sulfide concentration. ASTM Method D4658 utilizes an ion-selective electrode to determine sulfide ion in water.

EPA collected sulfide data for 236 samples in seven post-proposal sampling episodes using Methods 376.1, 376.2, and SM 4500E (EPA Episode numbers 6455, 6456, 6457, 6458, 6461, 6462, and 6463). These samples were collected from both process wastewaters prior to treatment and effluent wastewater after treatment. EPA reviewed the analytical data from these 236 samples and compared the three different methods. The study is included in the rulemaking record (see Section 16.2 of the rulemaking record, DCN 16941) and a summary of the findings are in the notice of data availability (67 FR 38754; June 5, 2002).

The nominal quantitation limit for Method 376.1 and SM 4500E, which is also the lower limit of the measurement range, is 1.0 mg/L. The nominal quantitation limit for Method 376.2 and SM 4500D is 0.5 mg/L. The nominal quantitation limit for D4658, which is also the lower limit of the measurement range, is 0.04 mg/L. Rather than use different baseline values for the same pollutant, EPA used the 1.0 mg/L as the baseline value from Method 376.1 because the majority of the data were determined by this method.

B.4.19 EPA Method 160.2 and SM 2540D (Total Suspended Solids)

EPA determined total suspended solids (TSS) by Method 160.2. Industry determined TSS by SM 2540D. Both methods are approved at 40 CFR 136 under "residue-non-filterable." Method 160.2 and SM 2540D are gravimetric methods with a lower limit of the measurement range of 4 mg/L; this value is also the nominal quantitation limit. The nominal quantitation limit of 4 mg/L is the baseline value.

B.4.20 EPA Method 204.1 and 7041 (Antimony)

Industry determined antimony by Methods 204.1 and 7041. Method 204.1 is approved at 40 CFR 136. Method 7041 is from *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846). Although Method 7041 is not listed at 40 CFR 136, it is approved for analyses of samples under the RCRA regulations at 40 CFR 261. Method 204.1 utilizes direct-aspiration atomic absorption as the determinative technique to measure antimony. Method 7041 utilizes the furnace technique in conjunction with an atomic absorption spectrophotometer.

The nominal quantitation limit (also the lower limit of the measurement range) for Method 204.1 is 1.0 mg/L. The nominal quantitation limit (also the lower limit of the measurement range) for Method 7041 is 20 : g/L. Rather than use different baseline values for the same pollutant, EPA used the minimum level of 20 : g/L for antimony from Method 1620 as the baseline value, because this was the method that EPA used for the determination of antimony.

B.4.21 EPA Method 206.2 and 7060A (Arsenic)

Industry determined arsenic by Methods 206.2 and 7060A. Method 206.2 is approved at 40 CFR 136. Method 7060A is from *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846). Although Method 7060A is not listed at 40 CFR 136, it is approved for analyses of samples under the RCRA regulations at 40 CFR 261. Methods 206.2 and 7060A utilize the furnace technique in conjunction with an atomic absorption spectrophotometer.

The nominal quantitation limit (also the lower limit of the measurement range) for Method 206.2 and Method 7060A is 5.0 : g/L. Rather than use different baseline values for the same pollutant, EPA used the minimum level of 10 : g/L for arsenic from Method 1620 as the baseline value, because this was the method that EPA used for the determination of arsenic.

B.4.22 EPA Method 231.2 (Gold)

EPA determined gold by Method 231.2, since this parameter is only semiquantitatively analyzed by Method 1620. Method 231.2 is approved at 40 CFR 136. Method 231.2 utilizes the furnace technique in conjunction with an atomic absorption spectrophotometer. The nominal quantitation limit for gold, which is also the lower limit of the measurement range, is 5 : g/L. The nominal quantitation limit is also the baseline value.

B.4.23 EPA Method 239.1 (Lead)

Industry determined lead by Method 239.1, which is approved at 40 CFR 136. Method 239.1 utilizes direct-aspiration atomic absorption as the determinative technique to measure lead. The nominal quantitation limit of 0.1 mg/L is expressed in the method as the lower limit of the measurement range. Rather than use different baseline values for the same pollutant, EPA used the minimum level of 50 : g/L for lead from Method 1620 from the ICP technique, as the baseline value since this was the method that EPA used for the determination of lead.

B.4.24 EPA Methods 245.1 and 245.2 (Mercury)

Industry determined mercury by Methods 245.1 and 245.2, both of which are approved at 40 CFR 136. The methods utilize cold vapor atomic absorption as the determinative technique to measure mercury. The nominal quantitation limit for both methods is 0.2 : g/L, which is also expressed as the lower limit of the measurement range. The nominal quantitation limit matches the nominal quantitation limit from Method 1620, which EPA used to determine mercury. The nominal quantitation limit is the same as the baseline value of 0.2 : g/L.

B.4.25 EPA Method 265.2 (Rhodium)

EPA determined rhodium by Method 265.2, since this parameter is only semiquantitatively analyzed by Method 1620. Method 265.2 is approved at 40 CFR 136. Method 265.2 utilizes the furnace technique in conjunction with an atomic absorption spectrophotometer. The nominal quantitation limit for rhodium, which is also the lower limit of the measurement range, is 20 : g/L. The nominal quantitation limit is also the baseline value.

B.4.26 EPA Methods 270.2 and 7740 (Selenium)

Industry determined selenium by Methods 270.2 and 7740. Method 270.2 is approved at 40 CFR 136. Method 7740 is from *Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods* (SW-846). Although Method 7740 is not listed at 40 CFR 136, it is approved for analyses of samples under the RCRA regulations at 40 CFR 261. Methods 270.2 and 7740 utilize the furnace technique in conjunction with an atomic absorption spectrophotometer.

The nominal quantitation limit for Method 270.2 and Method 7740, which is also lower limit of the measurement range, is 5.0 : g/L. Rather than use different baseline values for the same pollutant, EPA used the minimum level of 5 : g/L for selenium from Method 1620 as the baseline value, since this was the method that EPA used for the determination of selenium.

B.4.27 EPA Method 272.1 (Silver)

Industry determined silver by Method 272.1, which is approved at 40 CFR 136. Method 272.1 utilizes direct-aspiration atomic absorption as the determinative technique to measure silver. The nominal quantitation limit of 0.1 mg/L is expressed in the method as the lower limit of the measurement range. Rather than use different baseline values for the same pollutant, EPA used the minimum level of 10 : g/L for silver from Method 1620 as the baseline value, since this was the method that EPA used for the determination of silver.

B.4.28 EPA Methods 279.1 and 7841 (Thallium)

Industry determined thallium by Methods 279.1 and 7841. Method 279.1 is approved at 40 CFR 136. Method 7841 is from *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846). Although Method 7841 is not listed at 40 CFR 136, it is approved for analyses of samples under the RCRA regulations at 40 CFR 261. Method 279.1 utilizes direct-aspiration atomic absorption as the determinative technique to measure thallium. Method 7841 utilizes the furnace technique in conjunction with an atomic absorption spectrophotometer.

The nominal quantitation limit for Method 279.1, which is also the lower limit of the measurement range, is 1.0 mg/L. The nominal quantitation limit for Method 7841, which is also the lower limit of the measurement range, is 5 : g/L. Rather than use different baseline values for the same pollutant, EPA used the minimum level of 10 : g/L for thallium from Method 1620 as the baseline value, since this was the method that EPA used for the determination of thallium.

B.4.29 EPA Methods 624 and 625 (Volatile Organics and Semivolatile Organics)

EPA included industry-supplied data from Methods 624 and 625, both of which are approved at 40 CFR 136. Methods 624 and 625 are GC/MS methods, similar to Methods 1624 and 1625, except that Methods 624 and 625 do not utilize isotope dilution. The nominal quantitation limits are expressed as the lower limit of the measurement range, typically the concentration of the lowest calibration standard. However, rather than use different baseline values for the same pollutants (Methods 624 and 625 have many of the same analytes as Methods 1624 and 1625), EPA used the minimum levels that are listed in Methods 1624 and 1625 as the baseline values, since these methods were used by EPA for the determination of volatile and semivolatile organic analytes.

B.4.30 EPA Method 630.1 (Ziram)

Ziram was determined by Method 630.1. There are no methods approved at 40 CFR 136 for ziram. In this method, the sample is digested with acid to yield CS₂ by hydrolysis of the dithiocarbamate moiety. The evolved CS₂ is extracted from the water with hexane and the extract is injected into a GC. The nominal quantitation limit was determined by a low-point calibration standard. The nominal quantitation limit for ziram is 10 : g/L and was used as the baseline value.

B.5 Analytical Method Development Efforts

Section 304(h) of the Clean Water Act directs EPA to promulgate guidelines establishing test procedures for the analysis of pollutants. These methods allow the analyst to determine the presence and concentration of pollutants in wastewater. The methods are used for compliance monitoring, for filing applications for the NPDES program under 40 CFR 122.21, 122.41, 122.44 and 123.25, and for the implementation of the pretreatment standards under 40 CFR 403.10 and 403.12. To date, EPA has promulgated methods for all conventional and toxic pollutants, and for some nonconventional pollutants.

Currently approved methods for metals and wet chemistry parameters are included in the table of approved inorganic test procedures at 40 CFR 136.3, Table I-B. Table I-C at 40 CFR 136.3 lists approved methods for measurement of nonpesticide organic pollutants, and Table I-D lists approved methods for the toxic pesticide pollutants and for other pesticide pollutants. Dischargers must use the test methods promulgated at 40 CFR 136.3 or incorporated by reference in the tables, when available, to monitor pollutant discharges from the metal products and machinery (MP&M) industry, unless specified otherwise in 40 CFR 413, 433, 438, 463, 464, 467, and 471, or by the permitting authority.

Table I-C does not include six of the MP&M semivolatile organic pollutants and one of the MP&M volatile organic pollutant that EPA is regulating in the rule. Although these pollutants are missing from Table I-C, the analyte list for Method 1624 contains the volatile organic pollutant and the analyte list for Method 1625 contains the six semivolatile organic pollutants. EPA promulgated both of these methods for use in Clean Water Act measurement programs at 40 CFR 136, Appendix A.

As a part of the rule, EPA will allow the use of modified versions of Methods 624 and 1624 for the determination of the additional volatile organic pollutant and modified versions of Methods 625 and 1625 for the determination of the additional six semivolatile organic pollutants.

The modifications to Methods 624, 625, 1624, and 1625 have been included in the Docket for the rule. The modifications to Methods 624, 625, 1624, and 1625 consist of text, performance data, and quality control (QC) acceptance criteria for the additional analytes. This information will allow a laboratory to practice the methods with the additional analytes as an integral part. EPA conducted an interlaboratory validation study on the modifications to these methods. The

data from the interlaboratory study and the proposed modifications to the method were made available for public comment in a notice of data availability (see Section B.4.18). EPA is promulgating these method modifications for monitoring MP&M industry wastewaters at 40 CFR 136 in the rule.

As part of the rule, the following pollutants will be added to their respective analyte lists for the MP&M industry only:

| Methods | Pollutant | CAS Number |
|----------------------|--------------------------|------------|
| EPA Methods 624/1624 | carbon disulfide | 75-15-0 |
| EPA Methods 625/1625 | aniline | 62-53-3 |
| EPA Methods 625/1625 | 3,6-dimethylphenanthrene | 1576-67-6 |
| EPA Methods 625/1625 | 2-isopropylnaphthalene | 2027-17-0 |
| EPA Methods 625/1625 | 1-methylfluorene | 1730-37-6 |
| EPA Methods 625/1625 | 2-methylnaphthalene | 91-57-6 |
| EPA Methods 625/1625 | 1-methylphenanthrene | 832-69-9 |

Table B-1**Analytical Methods and Baseline Values**

| Analyte | Method | CAS Number | Samples Collected and Analyzed by | Nominal Quantitation Value (mg/L) | Baseline Value (mg/L) |
|------------------------|-------------------------------|------------|-----------------------------------|-----------------------------------|-----------------------|
| Amenable Cyanide | 335.1 | C025 | EPA, Industry | 0.02 | 0.02 |
| Ammonia as Nitrogen | 350.2 | 766417 | EPA | 0.05 | 0.05 |
| | 350.3 | | | 0.03 | |
| Available Cyanide | OIA-1677 | C054 | EPA | 0.002 | 0.002 |
| BOD | 405.1 | C003 | EPA | 2.00 | 2.00 |
| Carbonaceous BOD | 5210B | C002 | | 2.00 | |
| Chemical Oxygen Demand | 410.1 | C004 | EPA | 50.00 | 5.00 ^a |
| | 410.2 | | | 5.00 | |
| | 410.4(automated) ^b | | | 3.00 | |
| | 410.4(manual) ^b | | | 20.00 | |
| Chloride | 325.3 | 16887006 | EPA | 1.00 | 1.00 |
| Fluoride | 340.2 | 16984488 | EPA | 0.10 | 0.10 |
| HEM, SGT-HEM | 1664 | C036, C037 | EPA, Industry | 5.00 | 5.00 |
| Hexavalent Chromium | 218.4 | 18540299 | EPA | 0.01 | 0.01 |
| | 3111A | | Industry | 0.01 | |
| | 3500D | | EPA | 0.01 | |
| Metals | 1620 | c | EPA | c | c |
| | 200.7 | c | Industry | c | c |
| pH | 150.1 | C006 | EPA | N/A | |
| | 4500H | | Industry | N/A | |
| Semivolatile Organics | 1625 | c | EPA | c | c |
| | 625 | | Industry | | |
| Sulfate | 375.2 | 14808798 | EPA | 3.00 | 1.00 |
| | 375.4 | | EPA, Industry | 1.00 | |
| Total Cyanide | 335.2 | 57125 | EPA, Industry | 0.02 | 0.02 |
| | 335.3 | | Industry | 0.005 | |
| TDS | 160.1 | C010 | EPA | 10.00 | 10.00 |
| | 2540C | | Industry | 10.00 | |
| TKN | 351.3 | C021 | EPA | 1.00 | 1.00 |
| TOC | 415.1 | C012 | EPA | 1.00 | 1.00 |
| Total Phenols | 420.1 | C020 | EPA | d | 0.05 |
| | 420.2 | | | d | |
| Total Phosphorus | 365.2 | 14265442 | EPA | 0.01 | 0.01 |
| | 365.3 | | | 0.01 | |

Table B-1 (Continued)

| Analyte | Method | CAS Number | Samples Collected and Analyzed by | Nominal Quantitation Value (mg/L) | Baseline Value (mg/L) |
|-------------------|--------|------------|-----------------------------------|-----------------------------------|-----------------------|
| Total Sulfide | 376.1 | 18496258 | EPA | 1.00 | 1.00 |
| | 376.2 | | | 0.10 | |
| | 4500D | | Industry | 0.50 | |
| | 4500E | | EPA | 1.00 | |
| | D4568 | | Industry | 0.04 | |
| TSS | 160.2 | C009 | EPA | 4.00 | 4.00 |
| | 2540D | | Industry | 4.00 | |
| Volatile Organics | 1624 | c | EPA | c | c |
| | 624 | | Industry | | |
| Ziram | 630.1 | 137304 | EPA | 0.01 | 0.01 |

^aThe baseline value was adjusted to reflect the lowest nominal quantitation limit of the titrimetric procedures (i.e., 410.1, 410.2, and 5220B). See Section B.4.6 for a detailed explanation.

^bMethod 410.4 lists two different quantitation limits that are dependent upon whether the automated or manual protocols were followed. The automated method limit =3 mg/L and the manual method limit =20 mg/L.

^cThe method analyzed a number of pollutants each with its own CAS number, baseline value, and nominal quantitation limit.

^dThe method does not have a required calibration range. The baseline value is based upon the most frequently reported sample-specific detection limit.

Appendix C

WASTEWATER CHARACTERISTICS

Appendix C

WASTEWATER CHARACTERISTICS

This appendix summarizes the characteristics of wastewater generated by unit operations evaluated for the final rule and discharged to wastewater treatment systems. The wastewaters characterized in this appendix can be grouped into the following types of wastewaters:

- c Hexavalent chromium-bearing wastewater;
- c Cyanide-bearing wastewater;
- c Oil-bearing and organic pollutant-bearing wastewaters;
- c Chelated metal-bearing wastewater; and
- c Metal-bearing wastewater.

EPA evaluated a number of unit operations for the May 1995 proposal, January 2001 proposal, and June 2002 NODA (see Tables 4-3 and 4-4). However, EPA selected a subset of these unit operations for regulation in the final rule (see Section 1.0). For this appendix, the term "proposed MP&M operations" means those operations evaluated for the two proposals, NODA, and final rule. The term "final MP&M operations" means those operations defined as "oily operations" (see Section 1.0, 40 CFR 438.2(f), and Appendix B to Part 438) and regulated by the final rule.

Sections C.1 through C.5 summarize, for each type of wastewater, analytical data obtained during the MP&M regulatory development process for unit operations and influents to the wastewater treatment systems. These subsections present the number of samples analyzed, the number of times each pollutant was detected, and the minimum, maximum, mean, and median pollutant concentrations. Oil-bearing and organic pollutant-bearing wastewaters are characterized in Section 5.0.

Analytical data from the MP&M sampling program, including data obtained from sanitation districts, facilities performing proposed MP&M operations, and MP&M industry trade associations, are in the sampling episode reports located in Sections 5.2 and 15.3 of the rulemaking record.

C.1 Hexavalent Chromium-Bearing Wastewater

Hexavalent chromium-bearing wastewater exhibits high concentrations of hexavalent chromium and may contain other metals, and generally has a low pH of approximately 2. Sections C.1.1 and C.1.2 present chromium data for process water and associated rinse water and for the influent to the chromium reduction process, respectively.

C.1.1 Process Water and Rinse Water

Hexavalent chromium is present in process bath wastewater from various unit operations (e.g., chromic acid anodizing, chromate conversion coating, and chromium electroplating). Table C-1 presents the number of samples collected and analyzed during EPA's sampling program for unit operations and associated rinses that generate hexavalent chromium-bearing wastewater.

Table C-1

Number of Process and Rinse Water Samples for Unit Operations That Generate Hexavalent Chromium-Bearing Wastewater

| Unit Operation | No. of Process Water Samples | No. of Rinse Water Samples |
|---|------------------------------|----------------------------|
| Acid Treatment with Chromium | 1 | 3 |
| Anodizing with Chromium | 2 | 7 |
| Chromate Conversion Coating (Or Chromating) | 16 | 23 |
| Electroplating with Chromium | 4 | 10 |
| Wet Air Pollution Control | 6 | NA |

Source: MP&M Sampling Program.

NA - Not applicable. No associated rinse.

The mean total and hexavalent chromium concentrations in process bath water from these operations are 24,120 milligrams per liter (mg/L) and 10.0 mg/L, respectively. In the associated rinses, the mean concentrations for total and hexavalent chromium are 156 mg/L and 10.3 mg/L, respectively. Table C-2 summarizes total and hexavalent chromium concentration data for the process bath water and rinse water samples with detected concentrations for the unit operations listed in Table C-1.

Table C-2

Chromium Concentration Data for Process Water and Rinse Water

| Source | Chromium Form | No. of Samples Analyzed | No. of Detects | Concentration (mg/L) | | | |
|---------------|---------------|-------------------------|----------------|----------------------|---------|--------|--------|
| | | | | Minimum | Maximum | Mean | Median |
| Process Water | Total | 29 | 29 | 0.045 | 139,000 | 24,120 | 2,990 |
| | Hexavalent | 2 | 1 | 10.0 | 10.0 | 10.0 | 10.0 |
| Rinse Water | Total | 43 | 43 | 0.22 | 1,762 | 156 | 12.8 |
| | Hexavalent | 6 | 6 | 2.1 | 21.2 | 10.3 | 8.0 |

Source: MP&M Sampling Program.

C.1.2 Influent to Chromium Reduction Process

Facilities performing proposed MP&M operations usually segregate hexavalent chromium-bearing wastewater and treat it in a chromium reduction unit before commingling it with other process wastewater for further treatment. This segregated wastewater requires preliminary treatment to reduce hexavalent chromium to trivalent chromium because the chemical precipitation systems typically used to treat the commingled wastewater do not effectively treat hexavalent chromium. Typical chrome treatment involves chromium reduction using sulfur dioxide, sodium bisulfite, sodium metabisulfite, peroxide, or ferrous sulfate (see Section 8.4.1). Table C-3 presents the total and hexavalent chromium concentration data for samples of the influent to the chromium reduction process collected during EPA's sampling program. The treatment influent typically represents several commingled wastestreams, most of which are rinses. The influent-to-treatment concentrations are typically lower than the concentrations of process and rinse water due to the number of high-flow, low-concentration rinses that are commingled prior to treatment.

Table C-3

Chromium Concentration Data for the Influent to the Chromium Reduction Process

| Form of Chromium | No. of Samples Analyzed | No. of Detects | Concentration (mg/L) | | | |
|---------------------|-------------------------|----------------|----------------------|---------|------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Total Chromium | 54 | 54 | 0.2 | 432 | 54.8 | 18.2 |
| Hexavalent Chromium | 21 | 18 | 0.027 | 20 | 6.7 | 4.0 |

Source: MP&M Sampling Program.

C.2 Cyanide-Bearing Wastewater

Cyanide-bearing wastewater exhibits high concentrations of cyanide and metals such as copper, cadmium, and zinc, and generally has a high pH of approximately 12. Electroplating baths usually are the source of the high concentrations of cyanide. Cyanide may be analyzed as total cyanide (i.e., all forms included), amenable cyanide (i.e., cyanide present in forms amenable to treatment using alkaline chlorination), or weak-acid-dissociable cyanide (i.e., cyanide that dissociates in a weak acid). Sections C.2.1 and C.2.2 present cyanide concentration data for cyanide-bearing wastewater generated in proposed MP&M operations and in the influent to the cyanide treatment processes, respectively.

C.2.1 Process Water and Rinse Water

Table C-4 presents the number of process and rinse water samples collected and analyzed during EPA's sampling program for proposed MP&M operations that generate cyanide-bearing wastewater.

Table C-4

Number of Process and Rinse Water Samples for Unit Operations That Generate Cyanide-Bearing Wastewater

| Unit Operation | No. of Process Water Samples | No. of Rinse Water Samples |
|---------------------------------|------------------------------|----------------------------|
| Alkaline Treatment with Cyanide | 2 | 4 |
| Electroplating with Cyanide | 11 ^a | 13 |
| Wet Air Pollution Control | 3 | NA |

Source: MP&M Surveys and MP&M Site Visits.

^aDoes not include one sample from a gold-cyanide electroplating bath that was analyzed only for metals.

NA - Not applicable. No associated rinse.

Cyanide is used as a complexing agent in electroplating and cleaning baths and is present in wastewater generated in the wet air pollution control systems. Table C-5 summarizes the total and amenable cyanide concentration data for the process water and rinse water samples with detected concentrations for the unit operations listed in Table C-4.

Table C-5

Cyanide Concentration Data for Process Water and Rinse Water

| Source | Cyanide Form | No. of Samples Analyzed | No. of Detects | Concentration (mg/L) | | | |
|---------------|--------------|-------------------------|----------------|----------------------|---------|--------|--------|
| | | | | Minimum | Maximum | Mean | Median |
| Process Water | Total | 15 | 15 | 2.6 | 100,000 | 16,521 | 5,200 |
| | Amenable | 1 | 0 | NA | NA | NA | NA |
| Rinse Water | Total | 17 | 17 | 0.054 | 135 | 38 | 12.7 |
| | Amenable | 3 | 3 | 61.5 | 135 | 100 | 104 |

Source: MP&M Sampling Program.

NA - Not applicable. No samples were analyzed for amenable cyanide.

C.2.1 Influent to Cyanide Treatment Process

Facilities performing proposed MP&M operations usually segregate cyanide-bearing wastewater generated and treat it in a cyanide reduction process before commingling it with other process wastewater for further treatment. This preliminary treatment prevents cyanide complexes from forming in the commingled wastewater. Typical cyanide treatment methods include alkaline chlorination with sodium hypochlorite or chlorine gas or ozone oxidation (see Section 8.4.3). These complexes decrease the effectiveness of chemical precipitation, the technology typically used to treat the commingled wastewater. Table C-6 summarizes the cyanide concentration data for the influent to cyanide treatment process. The treatment influent typically represents several commingled wastestreams, most of which are rinses. The influent-to-treatment concentrations are typically lower than the concentrations of process and rinse water due to the number of high-flow, low-concentration rinses that are commingled prior to treatment.

Table C-6

Cyanide Concentration Data for Influent to the Cyanide Treatment Process

| Form of Cyanide | No. of Samples Analyzed | No. of Detects | Concentration (mg/L) | | | |
|------------------|-------------------------|----------------|----------------------|---------|------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Total Cyanide | 101 | 98 | 0.024 | 1,110 | 50.7 | 6.1 |
| Amenable Cyanide | 70 | 65 | 0.01 | 394 | 34.4 | 3.15 |

Source: MP&M Sampling Program.

C.3 Oil-Bearing and Organic Pollutant-Bearing Wastewaters

Oil-bearing wastewater exhibits high concentrations of oil and concentrations of organic pollutants. Oil-bearing wastewater is classified as containing either free (floating) oils or oil/water emulsions. As previously discussed above, “oily operations” are defined and regulated in the final rule and described in Section 4.0. The wastewater from oily operations is characterized in Section 5.0. In addition, EPA collected data on two proposed MP&M operations (Bilge Water and Dry Dock) that also generate oil-bearing and organic pollutant-bearing wastewaters. EPA is not regulating these two operations as EPA excluded the proposed Shipbuilding Dry Dock Subcategory from the final rule (see Section 9.0). Sampling episode reports for the proposed Shipbuilding Dry Dock Subcategory are located in Sections 5.2 and 15.2 of the rulemaking record.

C.4 Chelated Metal-Bearing Wastewater

Chelated metal-bearing wastewater exhibits high concentrations of metals, usually copper or nickel. Section C.4.1 discusses the various unit processes that generate chelated metal-

bearing wastewater and presents process water and rinse water pollutant concentration data for those processes collected during EPA's sampling program. Section C.4.2 discusses the pollutant concentration data for the influent to chelation-breaking preliminary treatment systems.

C.4.1 Process Water and Rinse Water

Facilities performing proposed MP&M operations use chelating agents in unit operations to prevent metals from being precipitated in the process bath. Electroless plating processes and associated rinses are the most common proposed MP&M operations that generate chelated metal-bearing wastewater. Some cleaning operations also generate chelated metal-bearing wastewater.

To characterize process waters and associated rinse waters for proposed MP&M operations that use chelating agents, EPA collected 37 samples of electroless plating solutions and rinses from electroless nickel plating, or from electroless copper. The maximum concentration of nickel in the process water and the rinses was 7,530 mg/L and 378 mg/L, respectively. The maximum concentration of copper in the process water and the rinses was 14,200 mg/L and 138 mg/L, respectively. Only one sample of tin was taken from process water, which had a concentration of 3.8 mg/L. Other metals typically plated using electroless plating include gold, palladium, and cobalt.

C.4.2 Influent to Chelate-Breaking Preliminary Treatment System

Typical chemical precipitation and sedimentation treatment processes do not remove chelated metals; therefore, facilities performing proposed MP&M operations usually segregate and pretreat chelated metal-bearing wastewater to break down the metal chelates before commingling it with other metal-bearing wastewaters. Preliminary treatment may consist of chemical reduction using reducing agents such as sodium borohydride, hydrazine, dithiocarbamate (measured analytically as ziram) or sodium hydrosulfite; high pH precipitation using calcium hydroxide or ferrous sulfate; or filtering the chelated metals out of solution (see Section 8.4.4).

EPA measured copper in concentrations ranging from 570 to 700 mg/L in the influent to the preliminary treatment systems for electroless copper processes. EPA measured nickel in concentrations ranging from 0.149 to 480 mg/L in the influent to the preliminary treatment systems for electroless nickel processes. Copper and nickel electroless plating are the most prevalent electroless plating operations seen at facilities performing proposed MP&M operations.

C.5 Metal-Bearing Wastewater

All of the wastewaters generated in proposed MP&M operations can contain metals, including the wastewaters described in the previous subsections. Section C.5.1 discusses proposed MP&M operations not presented in the previous subsections that generate metal-bearing wastewater and presents pollutant concentration data for the process water and rinse water for those operations.

Section C.5.2 presents pollutant concentration data for the influent to chemical precipitation systems used to treat metal-bearing wastewater.

C.5.1 Process Water and Rinse Water

Table C-7 lists the proposed MP&M operations that generate metal-bearing wastewater and presents the number of samples of process water and rinse water collected and analyzed in EPA's sampling program for each unit operation.

Facilities performing proposed MP&M operations typically use metals in the process baths for unit operations such as electroplating and stripping. Tables C-8 and C-9 summarize the pollutant concentration data for process water and rinse water, respectively, collected during the MP&M sampling program for unit operations generating metal-bearing wastewater. As shown in the tables, the metal priority pollutants most frequently detected in samples of process water were copper, zinc, chromium, nickel, and lead. Nonconventional metal pollutants frequently detected include iron, magnesium, boron, barium, manganese, and aluminum. The process water and rinses also typically contained oil and grease, total suspended solids, and low concentrations of organic pollutants.

C.5.2 Influent to the Chemical Precipitation Treatment Systems

Typically, facilities performing proposed MP&M operations segregate their wastewaters by type and treat them in preliminary treatment systems. After preliminary treatment, facilities performing proposed MP&M operations usually commingle the wastewater with other process wastewater and treat the commingled wastewater in an end-of-pipe treatment system. Generally, the end-of-pipe treatment consists of chemical precipitation and sedimentation (see Section 8.5.1). When high concentrations of metals are present in the wastewater, sites may use preliminary batch chemical precipitation and sedimentation to ensure that the high concentrations do not cause an upset in the end-of-pipe treatment system. Facilities performing proposed MP&M operations may also contract haul concentrated baths to centralized waste treatment facilities. Table C-10 summarizes the pollutant concentration data obtained from sampling the influent to end-of-pipe chemical precipitation with sedimentation and chemical precipitation with membrane filtration systems for metal-bearing wastewater.

Table C-7

Number of Process Water and Rinse Water Samples Collected and Analyzed for Unit Operations That Generate Metal-Bearing Wastewater

| Unit Operation | No. of Process Water Samples^a | No. of Rinse Water Samples^a |
|--|---|---|
| Abrasive Jet Machining | 3 | 3 |
| Acid Treatment without Chromium | 27 | 65 |
| Anodizing without Chromium | 4 | 3 |
| Carbon Black Deposition | 2 | 3 |
| Chemical Milling | 4 | 9 |
| Chemical Conversion Coating without Chromium | 24 | 59 |
| Electrochemical Machining | 1 | 2 |
| Electroless Plating | 9 | 28 |
| Electrolytic Cleaning | 9 | 17 |
| Electroplating without Chromium or Cyanide | 24 | 48 |
| Electropolishing | 1 | 1 |
| Painting-immersion (Including Electrophoretic, "E-coat") | 1 | 6 |
| Photo Image Developing | 5 | 11 |
| Photoresist Applications | 0 | 0 |
| Plasma Arc Machining | 1 | 0 |
| Salt Bath Descaling | 0 | 4 |
| Solder Flux Cleaning | 1 | 4 |
| Solder Fusing | 0 | 3 |
| Stripping (paint) | 6 | 4 |
| Stripping (metallic coating) | 9 | 12 |

Source: MP&M Sampling Program.

^aUnit operations for which no samples were collected are rarely performed or were not observed at facilities performing proposed MP&M operations.

Table C-8

**Process Water Pollutant Concentration Data for Unit Operations That
Generate Metal-Bearing Wastewater**

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|-----------------------------|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Organic Priority Pollutants | | | | | | |
| 1,1-Dichloroethane | 41 | 0 | NA | NA | NA | NA |
| 1,1-Dichloroethene | 41 | 0 | NA | NA | NA | NA |
| 1,1,1-Trichloroethane | 41 | 0 | NA | NA | NA | NA |
| 2-Nitrophenol | 40 | 1 | 2.15 | 2.15 | 2.15 | 2.15 |
| 2,4-Dinitrophenol | 36 | 1 | 335 | 335 | 335 | 335 |
| 2,4-Dimethylphenol | 40 | 1 | 0.167 | 0.167 | 0.167 | 0.167 |
| 2,6-Dinitrotoluene | 41 | 2 | 0.605 | 6.98 | 3.79 | 3.79 |
| 4-Chloro-3-Methylphenol | 39 | 0 | NA | NA | NA | NA |
| 4-Nitrophenol | 39 | 1 | 14.1 | 14.1 | 14.1 | 14.1 |
| Acenaphthene | 41 | 0 | NA | NA | NA | NA |
| Acrolein | 40 | 1 | 0.591 | 0.591 | 0.591 | 0.591 |
| Anthracene | 41 | 0 | NA | NA | NA | NA |
| Bis(2-ethylhexyl) Phthalate | 41 | 12 | 0.012 | 18.2 | 3.10 | 0.291 |
| Butyl Benzyl Phthalate | 41 | 0 | NA | NA | NA | NA |
| Chlorobenzene | 41 | 4 | 0.011 | 1.56 | 0.414 | 0.041 |
| Chloroethane | 41 | 0 | NA | NA | NA | NA |
| Chloroform | 41 | 3 | 0.012 | 0.218 | 0.080 | 0.012 |
| Di-n-octyl Phthalate | 41 | 2 | 0.639 | 1.42 | 1.03 | 1.03 |
| Di-n-butyl Phthalate | 41 | 0 | NA | NA | NA | NA |
| Dimethyl Phthalate | 41 | 0 | NA | NA | NA | NA |
| Ethylbenzene | 41 | 2 | 0.020 | 2.91 | 1.46 | 1.46 |
| Fluoranthene | 41 | 0 | NA | NA | NA | NA |
| Fluorene | 41 | 0 | NA | NA | NA | NA |
| Isophorone | 41 | 0 | NA | NA | NA | NA |
| Methylene Chloride | 41 | 3 | 0.011 | 0.173 | 0.080 | 0.056 |
| N-Nitrosodimethylamine | 41 | 1 | 6.67 | 6.67 | 6.67 | 6.67 |

Table C-8 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|---|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Organic Priority Pollutants (continued) | | | | | | |
| Naphthalene | 41 | 2 | 0.024 | 0.208 | 0.116 | 0.116 |
| Phenanthrene | 41 | 0 | NA | NA | NA | NA |
| Phenol | 41 | 5 | 0.024 | 1,044 | 216 | 2.00 |
| Pyrene | 41 | 0 | NA | NA | NA | NA |
| Tetrachloroethene | 41 | 0 | NA | NA | NA | NA |
| Toluene | 41 | 2 | 0.014 | 0.032 | 0.023 | 0.023 |
| Trichloroethene | 41 | 6 | 0.010 | 0.058 | 0.026 | 0.023 |
| Metal Priority Pollutants | | | | | | |
| Antimony | 129 | 50 | 0.002 | 3.56 | 0.359 | 0.090 |
| Arsenic | 129 | 62 | 0.001 | 16.4 | 0.655 | 0.080 |
| Beryllium | 129 | 39 | 0.001 | 3.87 | 0.270 | 0.030 |
| Cadmium | 132 | 74 | 0.002 | 57,100 | 791 | 0.203 |
| Chromium | 132 | 115 | 0.007 | 108,000 | 1,952 | 1.87 |
| Copper | 132 | 124 | 0.009 | 141,000 | 2,885 | 7.24 |
| Lead | 132 | 83 | 0.002 | 4,880 | 120 | 2.62 |
| Mercury | 129 | 25 | 0.0003 | 0.032 | 0.003 | 0.0009 |
| Nickel | 131 | 109 | 0.007 | 84,623 | 3,091 | 5.89 |
| Selenium | 129 | 30 | 0.001 | 8.00 | 0.659 | 0.051 |
| Silver | 132 | 57 | 0.001 | 14.4 | 0.503 | 0.075 |
| Thallium | 129 | 18 | 0.001 | 3.48 | 0.411 | 0.019 |
| Zinc | 131 | 118 | 0.005 | 53,200 | 2,750 | 15.7 |
| Conventional Pollutants | | | | | | |
| BOD 5-Day (Carbonaceous) | 33 | 22 | 4.29 | 18,600 | 4,537 | 1,600 |
| Oil and Grease (as HEM) | 53 | 27 | 1.08 | 2,400 | 271 | 68.9 |
| Total Suspended Solids | 127 | 119 | 5.00 | 110,000 | 2,338 | 154 |
| Nonconventional Organic Pollutants | | | | | | |
| 1-Bromo-2-Chlorobenzene | 41 | 4 | 0.012 | 0.978 | 0.382 | 0.268 |
| 1-Bromo-3-Chlorobenzene | 41 | 4 | 0.031 | 0.490 | 0.193 | 0.126 |
| 1-Methylfluorene | 41 | 0 | NA | NA | NA | NA |
| 1-Methylphenanthrene | 41 | 0 | NA | NA | NA | NA |

Table C-8 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|--|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Nonconventional Organic Pollutants (continued) | | | | | | |
| 2-Butanone | 40 | 12 | 0.070 | 26.1 | 4.61 | 1.43 |
| 2-Hexanone | 41 | 1 | 5.02 | 5.02 | 5.02 | 5.02 |
| 2-Isopropyl-naphthalene | 41 | 0 | NA | NA | NA | NA |
| 2-Methylnaphthalene | 41 | 1 | 0.220 | 0.220 | 0.220 | 0.220 |
| 2-Propanone | 41 | 27 | 0.052 | 250 | 11.3 | 0.485 |
| 3,6-Dimethylphenanthrene | 41 | 0 | NA | NA | NA | NA |
| 4-Methyl-2-Pentanone | 41 | 5 | 0.052 | 159 | 32.0 | 0.187 |
| Acetophenone | 41 | 0 | NA | NA | NA | NA |
| Alpha-terpineol | 41 | 0 | NA | NA | NA | NA |
| Aniline | 41 | 4 | 0.015 | 0.335 | 0.145 | 0.115 |
| Benzoic Acid | 41 | 8 | 0.051 | 8,098 | 1,037 | 27.2 |
| Benzyl Alcohol | 41 | 4 | 0.012 | 0.278 | 0.103 | 0.061 |
| Biphenyl | 41 | 0 | NA | NA | NA | NA |
| Carbon Disulfide | 41 | 1 | 0.053 | 0.053 | 0.053 | 0.053 |
| Dibenzofuran | 41 | 1 | 0.140 | 0.140 | 0.140 | 0.140 |
| Dibenzothiophene | 41 | 0 | NA | NA | NA | NA |
| Diphenyl Ether | 41 | 0 | NA | NA | NA | NA |
| Diphenylamine | 41 | 0 | NA | NA | NA | NA |
| Hexanoic Acid | 41 | 5 | 0.012 | 31.5 | 9.12 | 0.763 |
| Isobutyl Alcohol | 41 | 0 | NA | NA | NA | NA |
| m-Xylene | 14 | 2 | 0.020 | 5.06 | 2.54 | 2.54 |
| m+p Xylene | 27 | 0 | NA | NA | NA | NA |
| Methyl Methacrylate | 41 | 4 | 0.181 | 0.797 | 0.586 | 0.682 |
| n-Decane | 41 | 1 | 3.51 | 3.51 | 3.51 | 3.51 |
| n-Docosane | 41 | 1 | 0.142 | 0.142 | 0.142 | 0.142 |
| n-Dodecane | 41 | 1 | 1.27 | 1.27 | 1.27 | 1.27 |
| n-Eicosane | 41 | 1 | 0.030 | 0.030 | 0.030 | 0.030 |
| n-Hexacosane | 41 | 1 | 0.106 | 0.106 | 0.106 | 0.106 |
| n-Hexadecane | 41 | 0 | NA | NA | NA | NA |
| n-Nitrosopiperidine | 41 | 0 | NA | NA | NA | NA |

Table C-8 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|--|--------------------------------------|----------------|----------------------|---------|--------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Nonconventional Organic Pollutants (continued) | | | | | | |
| n-Octadecane | 41 | 0 | NA | NA | NA | NA |
| n-Tetracosane | 41 | 1 | 0.097 | 0.097 | 0.097 | 0.097 |
| n-Tetradecane | 41 | 0 | NA | NA | NA | NA |
| n-Triacontane | 41 | 1 | 0.082 | 0.082 | 0.082 | 0.082 |
| n,n-Dimethylformamide | 41 | 3 | 0.032 | 0.123 | 0.064 | 0.036 |
| o-cresol | 41 | 2 | 0.023 | 0.195 | 0.109 | 0.109 |
| o-xylene | 27 | 0 | NA | NA | NA | NA |
| o+p Xylene | 14 | 2 | 0.910 | 2.01 | 1.46 | 1.46 |
| p-Cymene | 41 | 0 | NA | NA | NA | NA |
| p-Cresol | 41 | 3 | 0.011 | 0.513 | 0.192 | 0.054 |
| Pyridine | 41 | 0 | NA | NA | NA | NA |
| Styrene | 41 | 0 | NA | NA | NA | NA |
| Trichlorofluoromethane | 41 | 0 | NA | NA | NA | NA |
| Tripropyleneglycol Methyl Ether | 41 | 2 | 0.245 | 1.45 | 0.848 | 0.848 |
| Nonconventional Metal Pollutants | | | | | | |
| Aluminum | 131 | 107 | 0.042 | 34,900 | 1,112 | 3.39 |
| Barium | 129 | 102 | 0.001 | 259 | 4.24 | 0.096 |
| Boron | 130 | 106 | 0.022 | 17,800 | 659 | 1.32 |
| Calcium | 129 | 125 | 0.054 | 2,250 | 130 | 23.4 |
| Cobalt | 129 | 81 | 0.003 | 4,700 | 73.5 | 0.660 |
| Gold | 1 | 1 | 0.392 | 0.392 | 0.392 | 0.392 |
| Iron | 131 | 122 | 0.011 | 374,000 | 7,051 | 13.4 |
| Magnesium | 129 | 106 | 0.085 | 960 | 73.8 | 15.2 |
| Manganese | 132 | 110 | 0.001 | 4,790 | 106 | 0.767 |
| Molybdenum | 130 | 87 | 0.001 | 197 | 5.40 | 0.237 |
| Sodium | 129 | 125 | 1.25 | 383,000 | 17,905 | 1,164 |
| Tin | 132 | 82 | 0.004 | 22,670 | 930 | 0.984 |
| Titanium | 129 | 84 | 0.002 | 13,250 | 180 | 0.303 |
| Vanadium | 129 | 68 | 0.001 | 1,495 | 23.5 | 0.066 |

Table C-8 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|---|--------------------------------------|----------------|----------------------|-----------|---------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Other Nonconventional Pollutants | | | | | | |
| Ammonia as Nitrogen | 66 | 53 | 0.060 | 44,800 | 2,922 | 10.0 |
| Chemical Oxygen Demand (COD) | 60 | 56 | 83.0 | 600,000 | 32,426 | 7,400 |
| Chloride | 69 | 53 | 1.00 | 328,300 | 20,901 | 240 |
| Cyanide | 10 | 7 | 0.027 | 0.510 | 0.153 | 0.120 |
| Fluoride | 69 | 58 | 0.140 | 55,500 | 1,034 | 5.10 |
| Hexavalent Chromium | 36 | 5 | 0.008 | 0.430 | 0.104 | 0.025 |
| Sulfate | 105 | 89 | 1.56 | 755,000 | 36,919 | 808 |
| Total Dissolved Solids | 125 | 123 | 87.0 | 1,000,000 | 135,033 | 64,100 |
| Total Kjeldahl Nitrogen | 49 | 42 | 0.480 | 40,000 | 2,584 | 42.0 |
| Total Organic Carbon (TOC) | 49 | 48 | 4.71 | 54,000 | 7,492 | 1,245 |
| Total Petroleum Hydrocarbons (as SGT-HEM) | 51 | 9 | 6.00 | 352 | 88.2 | 14.1 |
| Total Phosphorus | 30 | 21 | 0.020 | 11,000 | 945 | 11.0 |
| Total Recoverable Phenolics | 52 | 35 | 0.006 | 135 | 7.78 | 0.330 |
| Total Sulfide | 17 | 0 | NA | NA | NA | NA |

Source: MP&M Sampling Program.

^aDue to budgetary constraints, EPA did not analyze all samples for all pollutants.

NA - Not applicable.

Table C-9

**Rinse Water Pollutant Concentration Data for Unit Operations That
Generate Metal-Bearing Wastewater**

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|-----------------------------|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Organic Priority Pollutants | | | | | | |
| 1,1-Dichloroethane | 91 | 0 | NA | NA | NA | NA |
| 1,1-Dichloroethene | 91 | 0 | NA | NA | NA | NA |
| 1,1,1-Trichloroethane | 91 | 0 | NA | NA | NA | NA |
| 2-Nitrophenol | 89 | 0 | NA | NA | NA | NA |
| 2,4-Dimethylphenol | 91 | 0 | NA | NA | NA | NA |
| 2,4-Dinitrophenol | 85 | 0 | NA | NA | NA | NA |
| 2,6-Dinitrotoluene | 91 | 0 | NA | NA | NA | NA |
| 4-Chloro-3-Methylphenol | 91 | 0 | NA | NA | NA | NA |
| 4-Nitrophenol | 88 | 0 | NA | NA | NA | NA |
| Acenaphthene | 91 | 0 | NA | NA | NA | NA |
| Acrolein | 87 | 0 | NA | NA | NA | NA |
| Anthracene | 91 | 0 | NA | NA | NA | NA |
| Bis(2-ethylhexyl) Phthalate | 91 | 10 | 0.011 | 0.281 | 0.064 | 0.019 |
| Butyl Benzyl Phthalate | 91 | 0 | NA | NA | NA | NA |
| Chlorobenzene | 91 | 0 | NA | NA | NA | NA |
| Chloroethane | 91 | 0 | NA | NA | NA | NA |
| Chloroform | 91 | 49 | 0.010 | 0.063 | 0.025 | 0.022 |
| Di-n-octyl Phthalate | 91 | 1 | 0.013 | 0.013 | 0.013 | 0.088 |
| Di-n-butyl Phthalate | 91 | 6 | 0.014 | 0.190 | 0.098 | 0.013 |
| Dimethyl Phthalate | 91 | 1 | 0.021 | 0.021 | 0.021 | 0.021 |
| Ethylbenzene | 91 | 2 | 0.021 | 0.028 | 0.024 | 0.024 |
| Fluoranthene | 91 | 0 | NA | NA | NA | NA |
| Fluorene | 91 | 0 | NA | NA | NA | NA |
| Isophorone | 91 | 0 | NA | NA | NA | NA |
| Methylene Chloride | 91 | 1 | 0.011 | 0.011 | 0.011 | 0.011 |
| n-Nitrosodiphenylamine | 91 | 0 | NA | NA | NA | NA |
| n-Nitrosodimethylamine | 91 | 0 | NA | NA | NA | NA |

Table C-9 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|---|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Organic Priority Pollutants (continued) | | | | | | |
| Phenanthrene | 91 | 0 | NA | NA | NA | NA |
| Phenol | 90 | 5 | 0.011 | 2.00 | 0.417 | 0.024 |
| Pyrene | 91 | 0 | NA | NA | NA | NA |
| Tetrachloroethene | 91 | 0 | NA | NA | NA | NA |
| Toluene | 91 | 0 | NA | NA | NA | NA |
| Trichloroethene | 91 | 3 | 0.010 | 0.018 | 0.015 | 0.015 |
| Metal Priority Pollutants | | | | | | |
| Antimony | 261 | 42 | 0.002 | 0.158 | 0.026 | 0.011 |
| Arsenic | 261 | 63 | 0.001 | 0.308 | 0.018 | 0.006 |
| Beryllium | 261 | 13 | 0.001 | 0.059 | 0.010 | 0.001 |
| Cadmium | 265 | 62 | 0.002 | 6.93 | 0.310 | 0.011 |
| Chromium | 265 | 155 | 0.002 | 21.6 | 0.761 | 0.052 |
| Copper | 265 | 235 | 0.003 | 507 | 14.0 | 0.154 |
| Lead | 265 | 90 | 0.002 | 81.0 | 3.52 | 0.066 |
| Mercury | 261 | 25 | 0.0002 | 0.004 | 0.001 | 0.0004 |
| Nickel | 263 | 172 | 0.002 | 437 | 20.0 | 0.115 |
| Selenium | 261 | 39 | 0.001 | 0.412 | 0.019 | 0.003 |
| Silver | 265 | 55 | 0.001 | 0.962 | 0.047 | 0.010 |
| Thallium | 261 | 19 | 0.001 | 0.039 | 0.006 | 0.001 |
| Zinc | 265 | 187 | 0.002 | 13,700 | 168 | 0.019 |
| Conventional Pollutants | | | | | | |
| BOD 5-Day (Carbonaceous) | 86 | 39 | 1.07 | 11,400 | 505 | 40.0 |
| Oil and Grease (as HEM) | 130 | 34 | 1.12 | 114 | 17.2 | 10.4 |
| Total Suspended Solids | 260 | 174 | 2.00 | 6,920 | 132 | 20.0 |
| Nonconventional Organic Pollutants | | | | | | |
| 1-Bromo-2-Chlorobenzene | 91 | 0 | NA | NA | NA | NA |
| 1-Bromo-3-Chlorobenzene | 91 | 0 | NA | NA | NA | NA |
| 1-Methylfluorene | 91 | 0 | NA | NA | NA | NA |
| 1-Methylphenanthrene | 91 | 0 | NA | NA | NA | NA |
| 1,4-Dioxane | 91 | 1 | 0.196 | 0.196 | 0.196 | 0.196 |

Table C-9 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|--|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Nonconventional Organic Pollutants (continued) | | | | | | |
| 2-Hexanone | 91 | 0 | NA | NA | NA | NA |
| 2-Isopropyl-naphthalene | 91 | 0 | NA | NA | NA | NA |
| 2-Methylnaphthalene | 91 | 0 | NA | NA | NA | NA |
| 2-Propanone | 91 | 13 | 0.052 | 11.5 | 1.51 | 0.097 |
| 3,6-Dimethylphenanthrene | 91 | 0 | NA | NA | NA | NA |
| 4-Methyl-2-Pentanone | 91 | 2 | 0.190 | 17.4 | 8.80 | 8.80 |
| Acetophenone | 91 | 0 | NA | NA | NA | NA |
| Alpha-Terpineol | 91 | 0 | NA | NA | NA | NA |
| Aniline | 91 | 0 | NA | NA | NA | NA |
| Benzoic Acid | 91 | 6 | 0.108 | 4.31 | 1.21 | 0.659 |
| Benzyl Alcohol | 91 | 2 | 0.014 | 0.014 | 0.014 | 0.014 |
| Biphenyl | 91 | 0 | NA | NA | NA | NA |
| Carbon Disulfide | 91 | 0 | NA | NA | NA | NA |
| Dibenzofuran | 91 | 0 | NA | NA | NA | NA |
| Dibenzothiophene | 91 | 0 | NA | NA | NA | NA |
| Diphenyl Ether | 91 | 1 | 0.013 | 0.013 | 0.013 | 0.013 |
| Diphenylamine | 91 | 0 | NA | NA | NA | NA |
| Hexanoic Acid | 91 | 1 | 0.015 | 0.015 | 0.015 | 0.015 |
| Isobutyl Alcohol | 91 | 0 | NA | NA | NA | NA |
| m-Xylene | 20 | 2 | 0.036 | 0.076 | 0.056 | 0.056 |
| m+p Xylene | 71 | 0 | NA | NA | NA | NA |
| Methyl Methacrylate | 91 | 0 | NA | NA | NA | NA |
| n-Decane | 91 | 0 | NA | NA | NA | NA |
| n-Docosane | 91 | 1 | 0.012 | 0.012 | 0.012 | 0.012 |
| n-Dodecane | 91 | 0 | NA | NA | NA | NA |
| n-Eicosane | 91 | 0 | NA | NA | NA | NA |
| n-Hexacosane | 91 | 2 | 0.037 | 0.434 | 0.236 | 0.236 |
| n-Hexadecane | 91 | 1 | 0.057 | 0.057 | 0.057 | 0.057 |
| n-Nitrosopiperidine | 91 | 0 | NA | NA | NA | NA |
| n-Octacosane | 91 | 1 | 0.041 | 0.041 | 0.041 | 0.041 |

Table C-9 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|--|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Nonconventional Organic Pollutants (continued) | | | | | | |
| n-Tetracosane | 91 | 1 | 0.018 | 0.018 | 0.018 | 0.018 |
| n-Tetradecane | 91 | 1 | 0.221 | 0.221 | 0.221 | 0.221 |
| n-Triacontane | 91 | 2 | 0.030 | 0.477 | 0.253 | 0.253 |
| n,n-dimethylformamide | 91 | 2 | 0.026 | 0.115 | 0.071 | 0.071 |
| o-Cresol | 91 | 0 | NA | NA | NA | NA |
| o-Xylene | 71 | 0 | NA | NA | NA | NA |
| o+p Xylene | 20 | 2 | 0.042 | 0.113 | 0.077 | 0.077 |
| p-Cymene | 91 | 0 | NA | NA | NA | NA |
| p-Cresol | 91 | 0 | NA | NA | NA | NA |
| Pyridine | 91 | 0 | NA | NA | NA | NA |
| Styrene | 91 | 0 | NA | NA | NA | NA |
| Trichlorofluoromethane | 91 | 0 | NA | NA | NA | NA |
| Tripropyleneglycol Methyl Ether | 91 | 1 | 8.48 | 8.48 | 8.48 | 8.48 |
| Nonconventional Metal Pollutants | | | | | | |
| Aluminum | 263 | 161 | 0.022 | 76.9 | 1.61 | 0.192 |
| Barium | 261 | 207 | 0.001 | 2.90 | 0.064 | 0.028 |
| Boron | 263 | 179 | 0.016 | 363 | 4.38 | 0.180 |
| Calcium | 261 | 255 | 0.033 | 361 | 30.7 | 23.0 |
| Cobalt | 261 | 58 | 0.001 | 12.4 | 0.945 | 0.014 |
| Gold | 2 | 1 | 6.88 | 6.88 | 6.88 | 6.88 |
| Iron | 263 | 196 | 0.003 | 2,810 | 58.8 | 0.334 |
| Magnesium | 261 | 240 | 0.067 | 130 | 9.22 | 7.56 |
| Manganese | 265 | 171 | 0.001 | 68.3 | 1.52 | 0.024 |
| Molybdenum | 263 | 80 | 0.002 | 13.4 | 0.341 | 0.017 |
| Sodium | 261 | 257 | 0.277 | 55,800 | 710 | 60.0 |
| Tin | 265 | 105 | 0.002 | 828 | 11.6 | 0.052 |
| Titanium | 261 | 80 | 0.001 | 18.1 | 0.762 | 0.015 |
| Vanadium | 261 | 35 | 0.001 | 1.10 | 0.108 | 0.010 |

Table C-9 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|---|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Other Nonconventional Pollutants | | | | | | |
| Amenable Cyanide | 3 | 3 | 0.340 | 1.97 | 1.05 | 0.830 |
| Ammonia as Nitrogen | 114 | 68 | 0.050 | 1,190 | 91.2 | 1.58 |
| Chemical Oxygen Demand (COD) | 107 | 84 | 5.20 | 20,400 | 614 | 44.0 |
| Chloride | 77 | 76 | 1.20 | 5,000 | 219 | 26.0 |
| Cyanide | 12 | 9 | 0.028 | 87.0 | 10.7 | 0.830 |
| Fluoride | 77 | 68 | 0.110 | 60.0 | 3.65 | 0.990 |
| Hexavalent Chromium | 90 | 17 | 0.011 | 0.063 | 0.023 | 0.019 |
| Sulfate | 163 | 158 | 1.64 | 7,120 | 306 | 54.0 |
| Total Dissolved Solids | 258 | 258 | 10.0 | 132,000 | 2,469 | 550 |
| Total Kjeldahl Nitrogen | 79 | 44 | 0.100 | 395 | 28.0 | 8.69 |
| Total Organic Carbon (TOC) | 129 | 114 | 1.16 | 6,110 | 230 | 12.0 |
| Total Petroleum Hydrocarbons (as SGT-HEM) | 129 | 7 | 5.25 | 13.0 | 7.86 | 7.75 |
| Total Phosphorus | 28 | 21 | 0.026 | 290 | 30.9 | 1.40 |
| Total Recoverable Phenolics | 100 | 42 | 0.005 | 2.85 | 0.192 | 0.013 |
| Total Sulfide | 45 | 0 | NA | NA | NA | NA |

Source: MP&M Sampling Data.

^aDue to budgetary constraints, EPA did not analyze all samples for all pollutants.

NA - Not applicable.

Table C-10

**Pollutant Concentration Data for the Influent
to Chemical Precipitation Systems**

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|-----------------------------|--------------------------------------|----------------|----------------------|---------|--------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Organic Priority Pollutants | | | | | | |
| 1,1-Dichloroethane | 171 | 0 | NA | NA | NA | NA |
| 1,1-Dichloroethylene | 171 | 2 | 0.011 | 0.748 | 0.379 | 0.379 |
| 1,1,1-Trichloroethane | 171 | 6 | 0.019 | 0.084 | 0.053 | 0.053 |
| 2,4-Dimethylphenol | 162 | 0 | NA | NA | NA | NA |
| 2,4-Dinitrophenol | 167 | 2 | 0.111 | 1.66 | 0.885 | 0.885 |
| 2,6-Dinitrotoluene | 178 | 0 | NA | NA | NA | NA |
| 2-Nitrophenol | 177 | 0 | NA | NA | NA | NA |
| 4-Chloro-m-Cresol | 176 | 9 | 0.011 | 1.14 | 0.183 | 0.076 |
| 4-Nitrophenol | 172 | 0 | NA | NA | NA | NA |
| Acenaphthene | 178 | 0 | NA | NA | NA | NA |
| Acrolein | 141 | 0 | NA | NA | NA | NA |
| Anthracene | 178 | 1 | 0.104 | 0.104 | 0.104 | 0.104 |
| Benzyl Butyl Phthalate | 178 | 2 | 0.009 | 0.010 | 0.009 | 0.009 |
| Bis(2-ethylhexyl) Phthalate | 178 | 43 | 0.008 | 0.298 | 0.052 | 0.030 |
| Chlorobenzene | 171 | 0 | NA | NA | NA | NA |
| Chloroethane | 171 | 0 | NA | NA | NA | NA |
| Chloroform | 171 | 68 | 0.010 | 0.824 | 0.097 | 0.031 |
| Di-n-butyl Phthalate | 178 | 6 | 0.007 | 0.066 | 0.030 | 0.018 |
| Di-n-octyl Phthalate | 178 | 1 | 0.012 | 0.012 | 0.012 | 0.012 |
| Dimethyl Phthalate | 175 | 1 | 0.0004 | 0.0004 | 0.0004 | 0.0004 |
| Ethylbenzene | 171 | 5 | 0.006 | 0.335 | 0.074 | 0.010 |
| Fluoranthene | 178 | 0 | NA | NA | NA | NA |
| Fluorene | 178 | 1 | 0.045 | 0.045 | 0.045 | 0.045 |
| Isophorone | 175 | 0 | NA | NA | NA | NA |
| Methylene Chloride | 171 | 10 | 0.008 | 0.172 | 0.043 | 0.023 |
| n-Nitrosodimethylamine | 175 | 2 | 0.065 | 0.070 | 0.067 | 0.067 |

Table C-10 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|---|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Organic Priority Pollutants (continued) | | | | | | |
| Naphthalene | 178 | 3 | 0.012 | 0.054 | 0.035 | 0.038 |
| Phenanthrene | 178 | 3 | 0.041 | 0.112 | 0.071 | 0.060 |
| Phenol | 179 | 34 | 0.010 | 0.634 | 0.070 | 0.030 |
| Pyrene | 178 | 0 | NA | NA | NA | NA |
| Tetrachloroethene | 171 | 8 | 0.015 | 1.11 | 0.306 | 0.081 |
| Toluene | 171 | 6 | 0.009 | 2.77 | 0.534 | 0.019 |
| Trichloroethylene | 171 | 3 | 0.019 | 0.023 | 0.021 | 0.021 |
| Metal Priority Pollutants | | | | | | |
| Antimony | 261 | 86 | 0.002 | 1.13 | 0.058 | 0.018 |
| Arsenic | 268 | 109 | 0.001 | 0.530 | 0.025 | 0.009 |
| Beryllium | 268 | 64 | 0.0002 | 3.23 | 0.228 | 0.004 |
| Cadmium | 457 | 170 | 0.0003 | 323 | 4.25 | 0.039 |
| Chromium | 469 | 444 | 0.001 | 1,350 | 9.92 | 0.676 |
| Copper | 472 | 467 | 0.010 | 665 | 13.9 | 0.480 |
| Lead | 465 | 376 | 0.002 | 159 | 3.44 | 0.416 |
| Mercury | 266 | 52 | 0.00003 | 0.012 | 0.001 | 0.0003 |
| Nickel | 467 | 457 | 0.012 | 2,101 | 18.3 | 1.47 |
| Selenium | 265 | 42 | 0.001 | 0.090 | 0.018 | 0.006 |
| Silver | 460 | 222 | 0.001 | 4.94 | 0.406 | 0.036 |
| Thallium | 265 | 26 | 0.001 | 0.112 | 0.011 | 0.002 |
| Zinc | 472 | 459 | 0.009 | 636 | 33.6 | 3.65 |
| Conventional Pollutants | | | | | | |
| BOD 5-Day (Carbonaceous) | 133 | 86 | 2.40 | 609 | 64.4 | 26.0 |
| Oil and Grease (as HEM) | 236 | 159 | 0.570 | 32,000 | 428 | 12.1 |
| Total Suspended Solids | 334 | 314 | 4.00 | 11,400 | 803 | 120 |
| Nonconventional Organic Pollutants | | | | | | |
| 1,4-Dioxane | 166 | 6 | 0.033 | 2.41 | 0.788 | 0.584 |
| 1-Bromo-2-Chlorobenzene | 169 | 2 | 0.011 | 0.012 | 0.012 | 0.012 |
| 1-Bromo-3-Chlorobenzene | 169 | 5 | 0.026 | 0.067 | 0.045 | 0.038 |
| 1-Methylfluorene | 169 | 2 | 0.111 | 0.189 | 0.150 | 0.150 |

Table C-10 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|--|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Nonconventional Organic Pollutants (continued) | | | | | | |
| 2-Butanone | 166 | 13 | 0.056 | 2.45 | 0.668 | 0.151 |
| 2-Hexanone | 166 | 0 | NA | NA | NA | NA |
| 2-Isopropyl-naphthalene | 169 | 0 | NA | NA | NA | NA |
| 2-Methylnaphthalene | 173 | 2 | 0.076 | 0.205 | 0.140 | 0.140 |
| 2-Propanone | 166 | 87 | 0.051 | 16.7 | 0.822 | 0.137 |
| 3,6-Dimethylphenanthrene | 169 | 2 | 0.019 | 0.062 | 0.041 | 0.041 |
| 4-Methyl-2-Pentanone | 166 | 10 | 0.120 | 1.36 | 0.308 | 0.181 |
| Acetophenone | 169 | 2 | 0.010 | 0.011 | 0.011 | 0.011 |
| Alpha-terpineol | 162 | 5 | 0.013 | 0.087 | 0.051 | 0.054 |
| Aniline | 173 | 6 | 0.013 | 0.052 | 0.023 | 0.017 |
| Benzoic Acid | 173 | 69 | 0.011 | 34.8 | 3.27 | 0.229 |
| Benzyl Alcohol | 173 | 9 | 0.005 | 0.080 | 0.028 | 0.013 |
| Biphenyl | 169 | 1 | 0.011 | 0.011 | 0.011 | 0.011 |
| Carbon Disulfide | 166 | 10 | 0.016 | 3.92 | 0.505 | 0.058 |
| Dibenzofuran | 173 | 0 | NA | NA | NA | NA |
| Dibenzothiophene | 169 | 2 | 0.015 | 0.025 | 0.020 | 0.020 |
| Diphenyl Ether | 169 | 0 | NA | NA | NA | NA |
| Diphenylamine | 165 | 1 | 0.033 | 0.033 | 0.033 | 0.033 |
| Hexanoic Acid | 169 | 23 | 0.010 | 0.461 | 0.053 | 0.017 |
| Isobutyl Alcohol | 166 | 0 | NA | NA | NA | NA |
| m+p Xylene | 96 | 0 | NA | NA | NA | NA |
| m-Xylene | 70 | 1 | 0.016 | 0.016 | 0.016 | 0.016 |
| Methyl Methacrylate | 166 | 3 | 0.019 | 0.039 | 0.030 | 0.032 |
| n-Decane | 166 | 3 | 0.029 | 0.031 | 0.031 | 0.031 |
| n-Docosane | 169 | 6 | 0.011 | 0.026 | 0.016 | 0.013 |
| n-Dodecane | 168 | 6 | 0.044 | 0.772 | 0.269 | 0.101 |
| n-Eicosane | 169 | 17 | 0.010 | 0.181 | 0.034 | 0.020 |
| n-Hexacosane | 169 | 12 | 0.012 | 0.041 | 0.027 | 0.028 |
| n-Hexadecane | 169 | 22 | 0.010 | 0.631 | 0.085 | 0.026 |
| n-Nitrosopiperidine | 169 | 0 | NA | NA | NA | NA |

Table C-10 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|--|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Nonconventional Organic Pollutants (continued) | | | | | | |
| n-Octadecane | 169 | 25 | 0.011 | 0.493 | 0.072 | 0.024 |
| n-Tetracosane | 169 | 7 | 0.012 | 0.032 | 0.019 | 0.017 |
| n-Tetradecane | 169 | 14 | 0.016 | 1.01 | 0.174 | 0.058 |
| n-Triacontane | 169 | 4 | 0.011 | 0.031 | 0.019 | 0.017 |
| n,n-Dimethylformamide | 169 | 22 | 0.011 | 0.581 | 0.094 | 0.044 |
| o+p Xylene | 70 | 3 | 0.013 | 0.023 | 0.017 | 0.014 |
| o-Cresol | 169 | 0 | NA | NA | NA | NA |
| o-Xylene | 96 | 0 | NA | NA | NA | NA |
| p-Cresol | 169 | 10 | 0.013 | 0.030 | 0.019 | 0.017 |
| p-Cymene | 169 | 3 | 0.015 | 0.054 | 0.030 | 0.02 |
| Pyridine | 169 | 0 | NA | NA | NA | NA |
| Styrene | 173 | 8 | 0.010 | 0.188 | 0.041 | 0.022 |
| Trichlorofluoromethane | 171 | 6 | 0.029 | 0.109 | 0.045 | 0.033 |
| Tripropyleneglycol Methyl Ether | 169 | 23 | 0.064 | 5.21 | 1.83 | 1.05 |
| Nonconventional Metal Pollutants | | | | | | |
| Aluminum | 268 | 246 | 0.055 | 132 | 8.68 | 2.38 |
| Barium | 266 | 241 | 0.003 | 9.91 | 0.251 | 0.058 |
| Boron | 253 | 232 | 0.057 | 81.3 | 3.53 | 0.787 |
| Calcium | 268 | 268 | 3.40 | 1,220 | 83.0 | 34.9 |
| Cobalt | 264 | 121 | 0.001 | 25.8 | 0.757 | 0.019 |
| Gold | 20 | 10 | 0.013 | 0.150 | 0.056 | 0.038 |
| Iron | 268 | 268 | 0.022 | 3,880 | 111 | 5.38 |
| Magnesium | 268 | 263 | 0.349 | 3,360 | 74.5 | 8.88 |
| Manganese | 453 | 452 | 0.001 | 109 | 4.04 | 0.870 |
| Molybdenum | 453 | 347 | 0.001 | 3.06 | 0.175 | 0.037 |
| Sodium | 268 | 268 | 17.7 | 9,600 | 460 | 211 |
| Tin | 442 | 341 | 0.004 | 1,440 | 14.2 | 0.199 |
| Titanium | 253 | 189 | 0.002 | 76.4 | 1.53 | 0.048 |
| Vanadium | 264 | 87 | 0.002 | 1.19 | 0.052 | 0.014 |

Table C-10 (Continued)

| Pollutant | No. of Samples Analyzed ^a | No. of Detects | Concentration (mg/L) | | | |
|---|--------------------------------------|----------------|----------------------|---------|-------|--------|
| | | | Minimum | Maximum | Mean | Median |
| Other Nonconventional Pollutants | | | | | | |
| Ammonia as Nitrogen | 113 | 110 | 0.040 | 320 | 25.9 | 5.61 |
| Chemical Oxygen Demand (COD) | 203 | 194 | 1.50 | 13,000 | 532 | 122 |
| Chloride | 78 | 75 | 4.50 | 9,500 | 338 | 140 |
| Cyanide | 32 | 12 | 0.008 | 0.096 | 0.022 | 0.012 |
| Fluoride | 78 | 77 | 0.130 | 100 | 4.54 | 1.50 |
| Hexavalent Chromium | 133 | 50 | 0.010 | 21.0 | 0.771 | 0.060 |
| Sulfate | 177 | 170 | 18.0 | 6,125 | 469 | 318 |
| Total Dissolved Solids | 263 | 263 | 19.0 | 34,000 | 2,325 | 1,103 |
| Total Kjeldahl Nitrogen | 83 | 80 | 0.110 | 160 | 14.9 | 6.66 |
| Total Organic Carbon (TOC) | 175 | 146 | 3.57 | 400 | 73.5 | 46.9 |
| Total Petroleum Hydrocarbons (as SGT-HEM) | 143 | 52 | 5.00 | 93.0 | 20.4 | 10.0 |
| Total Phosphorus | 84 | 82 | 0.020 | 525 | 28.1 | 5.20 |
| Total Recoverable Phenolics | 188 | 110 | 0.006 | 13.0 | 0.387 | 0.047 |
| Total Sulfide | 95 | 31 | 0.150 | 28.0 | 5.20 | 1.03 |
| Ziram | 5 | 3 | 0.177 | 0.448 | 0.291 | 0.247 |

Source: MP&M Sampling Program.

^aDue to budgetary constraints, EPA did not analyze all samples for all pollutants.

NA - Not applicable.

Appendix D

POLLUTION PREVENTION AND WATER CONSERVATION PRACTICES

Appendix D

POLLUTION PREVENTION AND WATER CONSERVATION PRACTICES

EPA observed a number of pollution prevention and water conservation practices during site visits and sampling episodes, and MP&M surveys provided additional information on these practices (see Sections 3.0 and 8.0). Some common pollution prevention and water conservation methods for surface treatment include drag-out tanks, countercurrent cascade rinsing, manual and automatic rinse water shut-off, timed rinses, flow restrictors, conductivity meters, and in-process ion exchange and water recycle. In this appendix, EPA describes some of these common pollution prevention and water conservation methods used by facilities evaluated for the final rule (“MP&M facilities”) as a measure to assist a broader audience to achieve improved environmental performance and compliance, pollution prevention through source reduction, and continual improvement. **EPA is not promulgating or requiring any of these methods or mass-based limitations and standards in the MP&M effluent guidelines (see Section 15.0). The final limitations and standards in the MP&M effluent guidelines are concentration based and may be achieved using any method compliant with EPA regulations.**

D.1 Pollution Prevention and Water Conservation Practices for Surface Treatment

The Agency identified four categories of pollution prevention and water conservation practices and technologies that can be applied to reduce rinse-water use: drag-out reduction and/or drag-out recovery methods; improved rinse tank design and rinsing configurations; rinse-water use control devices; and, metal recovery and rinse-water reuse technologies. Surface treatment rinses include those following acid and alkaline treatment, anodizing, electroplating, electroless plating, and chemical conversion coating. Rinsing dilutes and removes the chemical film of drag-out remaining on parts and racks after processing in a chemical bath. In addition to conserving water use, some of these methods (especially those that affect drag-out and recover chemicals) also conserve raw materials, reduce pollutant loadings to wastewater treatment systems, and reduce treatment reagent requirements and sludge production. Within each of these categories are several specific practices and technologies. Table D-1 presents examples of these practices and technologies, as well as their applicability to the MP&M operations.¹ Table D-2 provides descriptions of these practices.

¹EPA evaluated a number of unit operations for the May 1995 proposal, January 2001 proposal, and June 2002 NODA (see Tables 4-3 and 4-4). However, EPA selected a subset of these unit operations for regulation in the final rule (see Section 1.0). For this Section, the term “proposed MP&M operations” means those operations evaluated for the two proposals, NODA, and final rule. The term “final MP&M operations” means those operations defined as “oily operations” (see Section 1.0, 40 CFR 438.2(f), and Appendix B to Part 438) and regulated by the final rule.

Table D-1

Potential Water Conservation Methods for Surface Treatment Rinses

| Practice | Alkaline Clean | Acid Clean | Hexavalent Chromium | Trivalent Chromium | Cadmium Zinc Cyanide | Cadmium Zinc Non-Cyanide | Acid Copper | Copper Cyanide | Watts, Woods, Other Nickels | Electro-less Nickel | Silver Cyanide | Gold Cyanide | Lead, Lead-Tin | Tin | Chrom-ate | Phos-phate | Chromic-AcidAnodize | Sulfuric Anodize |
|---|----------------|------------|---------------------|--------------------|----------------------|--------------------------|-------------|----------------|-----------------------------|---------------------|----------------|--------------|----------------|----------------|-----------|------------|---------------------|------------------|
| Drag-out Reduction and Recovery | | | | | | | | | | | | | | | | | | |
| Fog or spray rinsing over tank (110° F or higher) | ✓ | ✓ | ✓ | ✓ | | | | ✓ | ✓ | ✓ | | | | ✓ ^a | | ✓ | ✓ | |
| Controlled slow withdrawal | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Addition of wetting agent (when compatible) | | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Positioning work piece | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Long drip time | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Drip shield | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Air knife | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | | ✓ | ✓ | | | ✓ | ✓ | | ✓ |
| Drag-out tank (heated) | ✓ | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | |
| Drag-in/out tank | ✓ | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | |
| Lowest concentration | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Highest temperature | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Rinse Tank Design and Innovative Configuration | | | | | | | | | | | | | | | | | | |
| Countercurrent rinse | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Cascading rinse (cleaning) | ✓ | ✓ | | | | | | | | | | | | | | | | |
| Spray rinse | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Good tank design ^b | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Rinse Water Use Control | | | | | | | | | | | | | | | | | | |
| Flow restrictors | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Timer controls | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Conductivity controls | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |

Table D-1 (Continued)

| Practice | Alkaline Clean | Acid Clean | Hexavalent Chromium | Trivalent Chromium | Cadmium Zinc Cyanide | Cadmium Zinc Non-Cyanide | Acid Copper | Copper Cyanide | Watts, Woods, Other Nickels | Electro-less Nickel | Silver Cyanide | Gold Cyanide | Lead, Lead-Tin | Tin | Chrom-ate | Phos-phate | Chromic-AcidAnodize | Sulfuric Anodize |
|--|----------------|------------|---------------------|--------------------|----------------------|--------------------------|-------------|----------------|-----------------------------|---------------------|----------------|--------------|----------------|-----|-----------|------------|---------------------|------------------|
| Metal Recovery and Rinse Water Reuse Technologies | | | | | | | | | | | | | | | | | | |
| Evaporator ^c | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | ✓ | ✓ | ✓ | ✓ | ✓ | |
| Ion exchange ^c | | | | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | |
| Electrolytic Recovery | | | | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | | | |
| Electrodialysis ^c | | ✓ | | | ✓ | ✓ | | | ✓ | | | | | | | | | |
| Reverse osmosis ^c | | | | | ✓ | ✓ | ✓ | ✓ | ✓ | | | | ✓ | ✓ | ✓ | | | |

Source: MP&M Site Visits, MP&M Surveys, Technical Literature.

^a Alkaline tin only.

^b For example, air or other agitation, minimum size, and inlet, outlet location opposite ends.

^c Only common applications of this technology are checked.

Table D-2

**Descriptions of Pollution Prevention
and Water Conservation Practices and Technologies**

| Practice or Technology | Description |
|--------------------------------|--|
| Air Knife | Air knives are usually installed over a process tank or drip shield and are designed to remove drag-out by blowing it off the surface of parts and racks. Drag-out is routed back to the process tank. Air knives are more effective with flat parts. They cannot be used to dry surfaces that passivate or stain due to oxidation. |
| Cascade Rinsing | Cascade rinsing is a method of reusing rinse water. Water from one rinsing operation is plumbed to another, less critical one before being discharged to treatment. Some rinse waters acquire chemical properties, such as low pH, that make them desirable for reuse in specific rinse systems. This is generally referred to as reactive rinsing. |
| Conductivity Controller | <p>Conductivity probes measure the conductivity of water in a rinse tank to regulate the flow of fresh water into the rinse system. Conductivity controllers consist of a controller, a meter with adjustable set points, a probe that is placed in the rinse tank, and a solenoid valve. As parts are rinsed, dissolved solids are added to the water in the rinse tank, raising the conductivity of the water. When conductivity reaches the set point, the solenoid valve opens to allow make-up water to enter the tank. When the conductivity falls below the set point, the valve shuts to discontinue the make-up water.</p> <p>In theory, conductivity control of rinse flow is a precise method of maintaining optimum rinsing conditions in intermittently used rinse operations. In practice, conductivity controllers work best with deionized rinse water. Incoming water conductivity may vary day to day and season to season, which forces frequent set-point adjustments. Suspended solids and nonionic contaminants (e.g., oil) are not detected by the conductivity probe and can cause inadequate rinsing.</p> |
| Countercurrent Cascade Rinsing | Countercurrent cascade rinsing refers to a series of consecutive rinse tanks that are plumbed to cause water to flow from one tank to another in the direction opposite of the work flow. Countercurrent cascade rinsing is widely used to reduce the discharge rate of rinse water. Fresh water flows into the rinse tank located farthest from the process tank and overflows, in turn, to the rinse tanks closer to the process tank. This technique is termed countercurrent rinsing, because the part and the rinse water move in opposite directions. Over time, the first rinse becomes contaminated with drag-out and reaches a stable concentration that is lower than the process solution. The second rinse stabilizes at a lower concentration, which enables less rinse water to be used than if only one rinse tank were in place. The more countercurrent cascade rinse tanks (three-stage, four-stage, etc.), the less water is needed to adequately remove the process solution. |
| Drag-in/Drag-out Rinsing | A drag-in/drag-out rinse system may be a single tank or two tanks plumbed together. Parts enter the rinse system before and after processing in the bath. As parts enter the process bath, they drag in process chemicals present in the drag-in/drag-out rinse rather than plain rinse water. This rinsing configuration is an effective recovery method for process baths that have low evaporation rates. |

Table D-2 (Continued)

| Practice or Technology | Description |
|------------------------|---|
| Drag-out Tank | Drag-out tanks are rinse tanks that are initially filled with water and remain stagnant. Parts are rinsed in drag-out tanks directly after exiting the process bath. Gradually, the concentration of process chemicals in the drag-out tank rises. In the most efficient configuration, a drag-out tank is used after a heated process tank that has a moderate to high evaporation rate. Part of the fluid in the drag-out tank is returned to the process tank to replace the evaporative loss. The level of fluid in the drag-out tank is maintained by adding fresh water. |
| Drip Shields | Drip shields are installed between process tanks and rinse tanks to recover process fluid dripping off racks and barrels that would otherwise fall into rinse tanks or onto the floor. Often, drip shields are an inclined piece of polypropylene or other material that is inert to the process. |
| Drip Tanks | Drip tanks are similar to drag-out tanks except they are not filled with water. Parts exiting a process bath are held over the drip tank and the process fluid that drips from the parts is collected in the tank. When enough fluid is collected in the drip tank, it is returned to the process tank. Drip tanks are generally considered to be a less effective drag-out recovery practice than using drag-out tanks. |
| Electrodialysis | <p>Electrodialysis is a membrane technology used to remove impurities from and recover process solutions. With this technology, a direct current is applied across a series of alternating anion and cation exchange membranes to remove dissolved metal salts and other ionic constituents from solutions.</p> <p>An electrodialysis unit consists of a rectifier and a membrane stack. The stack consists of alternating anion- and cation-specific membranes that form compartments. As the feed stream enters the unit, each alternating membrane compartment becomes filled with either dilute or concentrate. When the compartments are filled, a direct current is applied across the membrane. Cations in a dilute compartment traverse one cation-specific membrane in the direction of the cathode, and are trapped in that compartment by the next membrane, which is anion-specific. Anions from the neighboring dilute compartment traverse the anion-specific membrane in the direction of the anode, joining the cations, and are likewise trapped in the concentrate compartment by the next cation-specific membrane. In this way, the feed stream is depleted of ions, and anions and cations are trapped in each concentrate compartment.</p> <p>The feed stream is often from the first rinse tank in a countercurrent series, with a concentration of 5 gallons per liter (g/L) or more of total dissolved solids (TDS). The concentrate, with a TDS concentration of 50 g/L or more and a volume of less than 10% of the feed stream, is returned to the process. The dilute, representing more than 90% of the feed stream at a TDS concentration of typically 1 g/L or less, is recycled as rinse water or discharged to treatment.</p> |

Table D-2 (Continued)

| Practice or Technology | Description |
|--|---|
| Electrolytic Recovery (Electrowinning) | <p>Electrolytic recovery is an electrochemical process used to recover metals from many types of process solutions, such as electroplating rinse waters and baths. Electrolytic recovery removes metal ions from a wastestream by processing the stream in an electrolytic cell, which consists of a closely spaced anode and cathode. Commercial equipment consists of several cells, a transfer pump, and a rectifier. Current is applied across the cell and metal cations are deposited on the cathodes. The wastestream is usually recirculated through the cell from a separate tank, such as a drag-out recovery rinse.</p> <p>Electrolytic recovery is typically applied to solutions containing nickel, copper, precious metals, and cadmium. Chromium and aluminum are poor candidates for electrolytic recovery. Drag-out recovery rinses and ion-exchange regenerant are common solutions that are processed using electrolytic recovery. Some solutions require pH adjustment prior to electrolytic recovery. Acidic, metal-rich, cation regenerant is an excellent candidate stream for electrolytic recovery, and is often electrolytically recovered without adjustment. In some cases, when the target concentration is reached, the wastestream is reused as cation regenerant.</p> |
| Evaporation | <p>Evaporation is a common chemical recovery technology. There are two basic types of evaporators: atmospheric and vacuum. Atmospheric evaporators, the more prevalent type, are relatively inexpensive to purchase and easy to operate. Vacuum evaporators are mechanically more sophisticated and are more energy-efficient. Vacuum evaporators are typically used when evaporation rates greater than 50 to 70 gallons/hour are required. Additionally, with vacuum evaporators, evaporated water can be recovered as a condensate and reused on site.</p> <p>A disadvantage of evaporation-based recovery is that all drag-out, including unwanted components, are returned and accumulate in the process bath. For this reason, deionized water is preferred as rinse water to prevent the introduction of water contaminants in the process bath.</p> |
| Flow Restrictor | <p>Flow restrictors prevent the flow in a pipe from exceeding a predetermined volume. They are commonly installed on a rinse tank's water inlet. These devices contain an elastomer washer that flexes under pressure to maintain a constant water flow regardless of pressure. Flow restrictors can maintain a wide range of flow rates, from less than 0.1 gal/min to more than 10 gal/min.</p> <p>As a stand-alone device, a flow restrictor provides a constant water flow. As such, for intermittent rinsing operations, a flow restrictor does not coordinate the rinse flow with drag-out introduction. Precise control with intermittent operations typically requires a combination of flow restrictors and rinse timers. However, for continuous rinsing (e.g., continuous electroplating machines), flow restrictors may be adequate for good water control.</p> |
| Fog or Spray Rinse Over Tank | <p>Fog or spray rinsing is performed over a process bath to recover drag-out. Draining over a process bath can be greatly enhanced by spray or fog rinsing, which dilutes and lowers the viscosity of the film of process fluid clinging to the parts. This method of drag-out recovery is only possible if the evaporation rate of the process fluid is moderate to high.</p> |

Table D-2 (Continued)

| Practice or Technology | Description |
|-----------------------------|--|
| Good Tank Design | <p>Rinse tanks should be designed to remove the drag-out layer from the part and cause it to rapidly and thoroughly mix with the rinse water. Common elements of good tank design are positioning the inlet and outlet at opposite ends of the tank, using air or other agitation, using a flow distributor, and using the minimum size tank possible.</p> |
| Ion Exchange | <p>Ion exchange is a reversible chemical reaction that exchanges ions in a feed stream for ions of like charge on the surface of an ion-exchange resin. Resins are broadly divided into cationic or anionic types. Typical cation resins exchange H^+ for other cations, while anion resins exchange OH^- for other anions.</p> <p>In practice, a feed stream is passed through a vessel, referred to as a column, which holds the resin. The feed stream is typically dilute rinse water. The exchange process proceeds until the capacity of the resin is reached (i.e., an exchange has occurred at all the resin facilities). A regenerant solution is then passed through the column. For cation resins, the regenerant is an acid, and the H^+ ions replace the cations captured from the feed stream. For anion resins, the regenerant is a base, and OH^- ions replace the anions captured from the feed stream. The concentration of feed stream ions is much higher in the regenerant than in the feed stream; therefore, the ion-exchange process accomplishes both separation and concentration.</p> <p>Ion exchange is used for water recycling and/or metal recovery. For water recycling, cation and anion columns are placed in series. The feed stream is deionized and the product water is reused for rinsing. Often, closed-loop rinsing is achieved. The regenerant from the cation column typically contains the metal species, which can be recovered in elemental form via recovery. The anion regenerant is typically discharged to wastewater treatment. When metal recovery is the only objective, a single or double cation column unit containing selective resin is used. These resins attract divalent cations while allowing monovalent cations to pass, a process usually referred to as metal scavenging. Water cannot be recycled because contaminants other than the target cations remain in the stream exiting the column.</p> |
| Long Drip Time | <p>Long drip times over the process tank reduce the volume of drag-out reaching the rinsing system. Automatic lines can be easily programmed to include optimum drip times. On manual lines, racks are commonly hung on bars over process baths and allowed to drip. Barrels can be rotated over the process bath to enhance drainage. Some surfaces cannot tolerate long exposure to air due to oxidation or staining, and would therefore be unsuitable for extended drip times.</p> |
| Raising Bath Temperature | <p>Bath temperature and viscosity are inversely related. Operating at the highest possible bath temperature lowers viscosity and reduces drag-out. Higher bath temperatures also increase evaporation, which facilitates efficient recovery rinsing.</p> |
| Lowering Bath Concentration | <p>Operating at the lowest possible concentration reduces the mass of chemicals in a given volume of drag-out. Also, viscosity and concentration are directly related and lower process bath concentration lowers viscosity and reduces drag-out volume. Contaminants and other substances that build in concentration over the life of a process bath should be controlled at a low level, if possible.</p> |
| Part Position on Rack | <p>Positioning parts on racks to promote rapid draining includes minimizing the profile of the parts emerging from the bath, tilting and inverting cup-shaped parts, and avoiding placement of parts directly atop one another.</p> |

Table D-2 (Continued)

| Practice or Technology | Description |
|------------------------|---|
| Slow Part Withdrawal | <p>The faster a part is removed from a process bath, the thicker the layer of fluid clinging to the part will be. A slower withdrawal rate reduces the thickness of the fluid layer and reduces drag-out. Generally, this method of drag-out reduction can only be practiced on automatic lines where the withdrawal velocity can be programmed.</p> |
| Reverse Osmosis | <p>Reverse osmosis is a membrane separation technology used for chemical recovery. The feed stream, usually relatively dilute rinse water or wastewater, is pumped to the surface of the reverse osmosis membrane at pressures of 400 to 1,000 psig. The membrane separates the feed stream into a reject stream and a permeate. The reject stream, containing most of the dissolved solids in the feed stream, is deflected from the membrane while the permeate passes through. Reverse osmosis membranes reject more than 99% of multivalent ions and 90% to 96% of monovalent ions, in addition to organic pollutants and nonionic dissolved solids. The permeate stream is usually of sufficient quality to be recycled as rinse water, despite the small percentage of monovalent ions (commonly potassium, sodium and chloride) that pass through the membrane.</p> <p>A sufficiently concentrated reject stream can be returned directly to the process bath. The reject stream concentration can be increased by recycling the stream through the unit more than once or by increasing the feed pressure. In multiple-stage units containing more than one membrane chamber, the reject stream from the first chamber is routed to the second, and so on. The combined reject streams from multistage units may, in some cases, have high enough concentrations to be returned directly to the bath.</p> |
| Timer Rinse Controller | <p>Rinse timers are electronic devices that control a solenoid valve. The timer usually consists of a button that, when pressed, opens the valve for a predetermined length of time, usually from 1 to 99 minutes. When the valve is open, make-up water is allowed to flow into a given tank. After the time period has expired, the valve is automatically shut. The timer may be activated either manually by the operator or automatically by the action of racks or hoists.</p> <p>Most rinse systems that are used intermittently benefit from the installation of a rinse timer, as operator error is eliminated. Rinse timers installed in conjunction with flow restrictors can provide precise control when the incoming water pressure may rise and fall. Rinse timers are less effective in continuous or nearly continuous rinse operations (e.g., continuous electroplating machines).</p> |
| Wetting Agents | <p>Wetting agents or surfactants may be added to some process baths to reduce viscosity and surface tension, thereby significantly reducing drag-out.</p> |

Source: MP&M Site Visits, MP&M Surveys, Technical Literature.

D.1.1 Drag-Out Reduction and Drag-Out Recovery

The quantity of water needed for good rinsing for a given system is proportional to the quantity of drag-out from a process bath. Facilities can implement various methods that minimize the rate of drag-out (measured as gallons per square foot of part surface area) and/or they can implement direct drag-out recovery. The drag-out rate for an individual process operation (e.g., cleaning or plating) depends on numerous factors, including process type, shape of parts processed, production equipment, and processing procedures, which include human factors. Of these factors, the shape of the parts and the type of device used to move the parts (e.g., racks, baskets, barrels) usually have the greatest influence on drag-out rates. Tables D-3 and D-4 present drag-out rate estimates from two sources in the literature for various shaped parts.

Table D-3

Average Drag-Out Losses - from Soderberg's Work

| Nature of Work Drainage | Drag-Out Rate (gal/1,000 ft²) |
|--------------------------------|---|
| Vertical | |
| Well drained | 0.4 |
| Poorly drained | 2 |
| Very poorly drained | 4 |
| Horizontal | |
| Well drained | 0.8 |
| Very poorly drained | 10 |
| Cup Shapes | |
| Well drained | 8 |
| Very poorly drained | 24 |

Source: Reference 4.

Table D-4**Average Drag-Out Losses - from Hogaboom's Work**

| Electroplating Solution Type | Drag-Out Rate (gal/1,000 ft ²) | |
|-----------------------------------|--|--------------------|
| | Flat Surfaces | Contoured Surfaces |
| Brass | 0.95 | 3.3 |
| Cadmium | 1 | 3.1 |
| Chromium (33 oz/gal) | 1.18 | 3 |
| Chromium (53 oz/gal) ^a | 4.53 | 11.9 |
| Copper cyanide | 0.91 | 3.2 |
| Watts nickel | 1 | 3.8 |
| Silver | 1.2 | 3.2 |
| Stannate tin | 0.83 | 1.6 |
| Acid zinc | 1.3 | 3.5 |
| Cyanide zinc | 1.2 | 3.8 |

Source: Reference 4.

^aIncreased viscosity, caused by an increase in concentration, can increase the drag-out volume approximately three times with less than double the concentration increase.

Several factors other than shape, some of which are interrelated, influence the drag-out rate for a given process and part. Table D-5 lists these and other key factors and describes their impact on drag-out rates. Also listed are examples of water conservation practices that reduce the generation of drag-out, and the major restrictions that are associated with these practices. Table D-6 shows the effect of altering the withdrawal rate and drain time.

Soderberg's data indicate that the shape of the part has a significant influence on drag-out rate. Cup-shaped parts, including intricately designed parts with internal surfaces, can generate five or more times the drag-out than flat surfaced parts with the same surface area. Hogaboom's data show a similar trend for flat versus contoured surfaces. These data also show that the type and concentration of the electroplating solution influence the drag-out rate. For example, some solutions, such as stannate tin, drain effectively, while others, such as concentrated chromium electroplating solutions (53 ounces per gallon (oz/gal) drain poorly. As to the type of device used to move parts, barrels (used to hold fasteners or other small parts that cannot be practically held by racks) generate more drag-out than racks, because of the surface area of the barrel and its tendency to hold the solution.

Table D-5**Factors Affecting Drag-Out**

| Factor Affecting Drag-Out | Impact on Drag-out | Potential Pollution Prevention and Water Conservation Practices | Restrictions |
|----------------------------------|---|--|--|
| Bath Concentration | Concentration and drag-out are directly related. | Operate at lowest concentration possible. Remove all contaminants promptly. | Concentration range limited by process. |
| Bath Temperature | Higher temperatures lower drag-out by lowering viscosity. | Operate at highest possible temperature. | Temperature range limited by process. |
| Bath Viscosity | High viscosity raises drag-out by increasing the thickness of the fluid layer clinging to the part. | Operate at highest temperature and lowest concentration possible. Add wetting agent. | Concentration and temperature ranges limited by process. Wetting agent must be compatible. |
| Part Configuration | Cup shapes result in 8-20 times the drag-out volume of flat shapes. | Drain holes can be added to many cup-shaped parts to improve drainage of drag-out. | Functionality of parts may restrict use of drain holes or other changes to part configuration. |
| Part Orientation | Orientation on rack can be optimized to minimized drag-out. | Keep records of optimal orientations. Train operators. | None. |
| Withdrawal Rate | Doubling speed of withdrawal results in a fourfold increase in drag-out volume. | Program automatic equipment for slow withdrawal. | Impossible to consistently practice without automation. |
| Drain Time | Long drain times and barrel rotations greatly reduce drag-out. | Program automatic equipment for long drain times. | Impossible or difficult to consistently practice without automation. Drain time limited by staining or passivation of some coatings. |
| Rack versus Barrel | Barrels produce greater drag-out than racks. | (See "Rack/Barrel Design") | Part transport device is dictated by part size. |
| Rack/Barrel Design | Drag-out volume is related to barrel design. | Redesign barrels with largest holes possible. | Barrel design limited by part sizes and configurations. |
| Rack/Barrel Condition | Loose rack coating cause reservoirs of fluid to be transported with rack. | Maintain a schedule of maintenance and recoating. | None. |
| Operator Awareness | Poor operator awareness greatly increases drag-out or offsets other practices. | Require training programs for operators. | None. |

Source: MP&M Site Visits, MP&M Surveys, Technical Literature.

Table D-6**Effect of Withdrawal Rate and Drain Time on Drag-out Rate^a**

| Micro-Etch Results | Withdrawal Rate (ft/min) | Time of Withdrawal (seconds) | Drain Time (seconds) | Total Time (seconds) | Drag-out (gal/1,000 ft²) |
|--|---------------------------------|-------------------------------------|-----------------------------|-----------------------------|--|
| Baseline | 100 | 1.7 | 3.4 | 5.1 | 3.13 |
| Slower rate of withdrawal | 11 | 14.9 | 2.5 | 17.4 | 1.73 |
| Intermediate withdrawal rate and longer drain time | 40 | 4.3 | 12.1 | 16.4 | 1.83 |

| Electroless Copper Results | Withdrawal Rate (ft/min) | Time of Withdrawal (seconds) | Drain Time (seconds) | Total Time (seconds) | Drag-out (gal/1,000 ft²) |
|--|---------------------------------|-------------------------------------|-----------------------------|-----------------------------|--|
| Baseline | 94 | 1.8 | 5.2 | 7 | 1.55 |
| Slower Rate of Withdrawal | 12 | 13.9 | 3.2 | 17 | 0.78 |
| Intermediate Withdrawal Rate and Longer Drain Time | 40 | 4.3 | 11.9 | 16.3 | 0.75 |

Source: Reference 4.

^aThe effects of changing the withdrawal rate and drain time were measured at a printed circuit board manufacturing facility.

The following is a list of drag-out reduction practices that facilities can implement on electroplating or surface finishing lines:

- Lower process solution viscosity and/or surface tension by decreasing chemical concentration, increasing bath temperature, or using wetting agents;
- Reduce drag-out volume by modifying rack/barrel design and perform rack maintenance to avoid solution trapping;
- Position parts on racks in a manner that avoids trapping solution;
- Reduce speed of rack/barrel withdrawal from process solution and/or increase dwell time over process tank;
- Rotate barrels over the process tank to improve drainage;
- Use spray/fog rinsing over the process tank (limited applicability);
- Use drip boards and return process solution to the process tank;

- Use drag-out tanks, where applicable, and return solution to the process tank; and
- Work with customers to ensure that part design maximizes drainage.

D.1.2 Improved Rinse Tank Design and Rinsing Configurations

Rinse tank design and rinsing configuration greatly influence water usage. The key objectives for optimal rinse tank design are to quickly remove drag-out from the part and completely disperse the drag-out throughout the rinse tank. Achieving these objectives reduces the time necessary for rinsing and minimizes the concentration of contaminants on the part when it leaves the rinse tank. Examples of good design include locating water inlet and discharge points of the tank at opposite positions in the tank to avoid short-circuiting, and using air agitation for better mixing (5).

Various rinsing configurations are used by MP&M facilities. Having single-rinse tanks following each process tank is the most inefficient use of rinse water. Multiple-rinse tanks connected in series (i.e., countercurrent cascade rinsing) reduces the water needs of a given rinsing operation by one or more orders of magnitude. Spray rinsing can also reduce water use requirements, but the achievable percent reduction is usually less than for countercurrent cascade rinsing. Other configurations that reduce water use include cascade, reactive, and dual purpose rinses.

D.1.3 Rinse Water Use Control Devices

Regardless of the type of rinsing configuration used, facilities can reduce their water use by coordinating water use and water use requirements. Matching water use to water use requirements can optimize the quantity of rinse water used for a given work load and tank arrangement (5). Not controlling water use negates the benefits of using multiple rinse tanks or other water conservation practices and increases water usage.

Facilities may wish to implement at least one effective method of water use control on all electroplating or surface finishing lines. Effective water use controls include, but are not limited to:

- Use of softened or deionized water for rinsing.
- Flow restrictors (flow restrictors as a stand-alone method of rinse water control are only effective with plating lines that have constant production rates, such as automatic plating machines. For other operations, there must also be a mechanism or procedure for stopping water flow during idle periods.).
- Conductivity controls.

- Timer rinse controls.
- Production-activated controls (e.g., spray systems activated when a rack or barrel enters/exits a rinse station).

D.1.4 Metal Recovery and Rinse Water Reuse Technologies

MP&M facilities use various technologies to recover metals drag-out and rinses and reuse the rinse water. The technologies most commonly used are evaporation, ion exchange, electrolytic recovery (also referred to as electrowinning), reverse osmosis, and electrodialysis. Table D-7 presents examples of metal recovery technologies and the drag-out/rinses to which they are primarily applied.

Table D-7

Examples of Metal Recovery Methods

| Chemistry or Process with Which Rinse is Associated | Recovery Technology |
|--|--|
| Brass electroplating | Electrolytic recovery, evaporation |
| Cadmium (cyanide) electroplating | Electrodialysis, electrolytic recovery, evaporation, ion exchange, reverse osmosis |
| Cadmium (noncyanide) electroplating | Electrodialysis, electrolytic recovery, evaporation, ion exchange, reverse osmosis |
| Chromate conversion coating of aluminum | Evaporation |
| Chromium (hard) anodizing | Evaporation, mist eliminator |
| Chromium electroplating - decorative (Cr+6) | Evaporation |
| Chromium electroplating - decorative (Cr+3) | Evaporation |
| Copper (cyanide and sulfate) electroplating | Electrolytic recovery, evaporation, ion exchange, reverse osmosis |
| Gold electroplating | Electrolytic recovery, ion exchange |
| Lead-tin electroplating | Evaporation, ion exchange |
| Nickel electroplating | Electrodialysis, electrolytic recovery, evaporation, ion exchange, reverse osmosis |
| Nickel electroless plating | Evaporation, ion exchange |
| Nickel sealant | Reverse osmosis |
| Silver electroplating | Electrolytic recovery, evaporation, ion exchange |
| Zinc (cyanide) electroplating | Electrolytic recovery, evaporation, reverse osmosis |
| Zinc (noncyanide) electroplating | Electrolytic recovery, evaporation, ion exchange, reverse osmosis |
| Zincate | Evaporation |

Source: Reference 5.

D.1.5 Summary of Water Conservation Methods

Figures D-1(a) through (f) present six examples of rinsing configurations with increasingly good levels of water use practices. Each of these rinse systems is described below. These configurations can be operated to provide adequate rinsing and are common at MP&M facilities. However, the quantity of water needed for the same rinse quality may vary by as much as two orders of magnitude from the lowest level to the best level of water use.

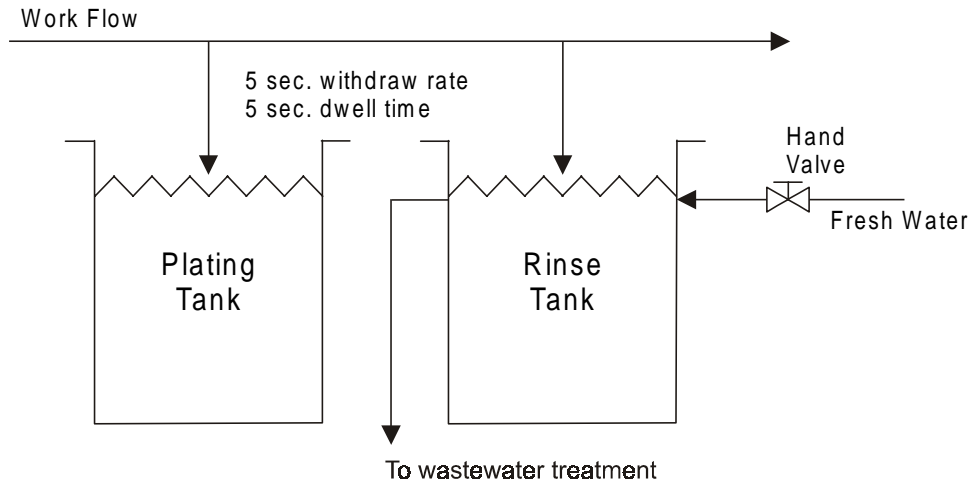


Figure D-1(a). Single Rinse Tank

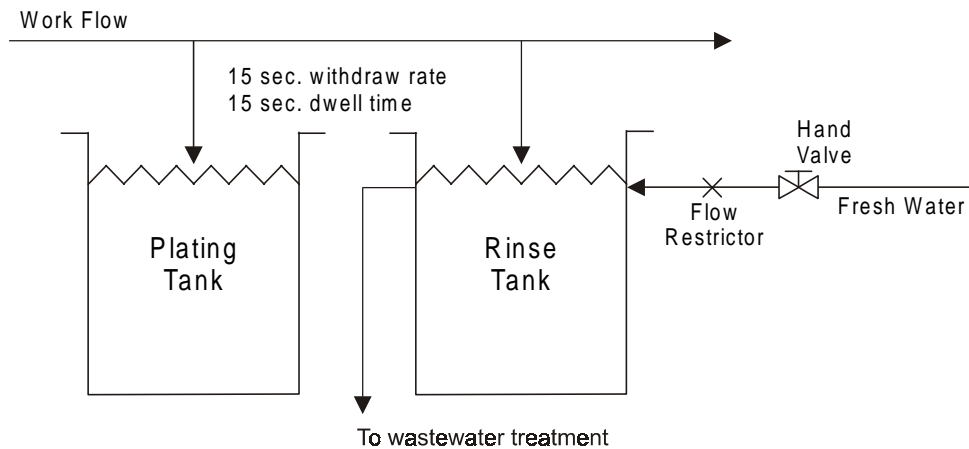


Figure D-1(b). Single Rinse Tank with Flow Reduction

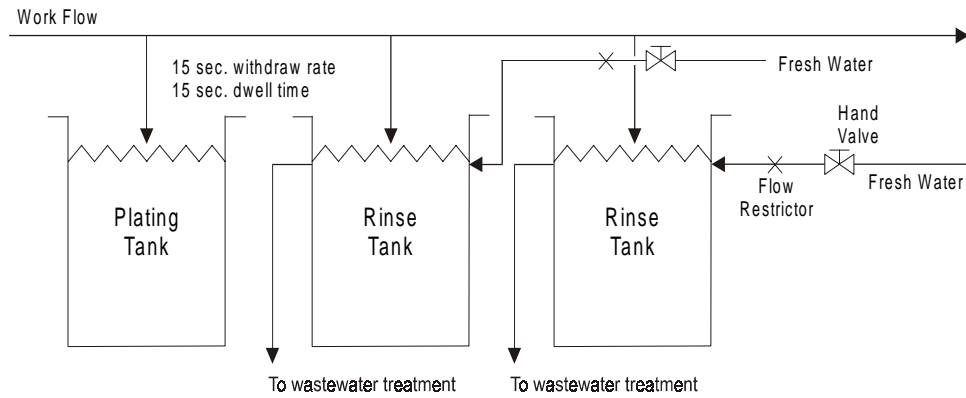


Figure D-1(c). Multiple Rinse Tanks with Flow Reduction

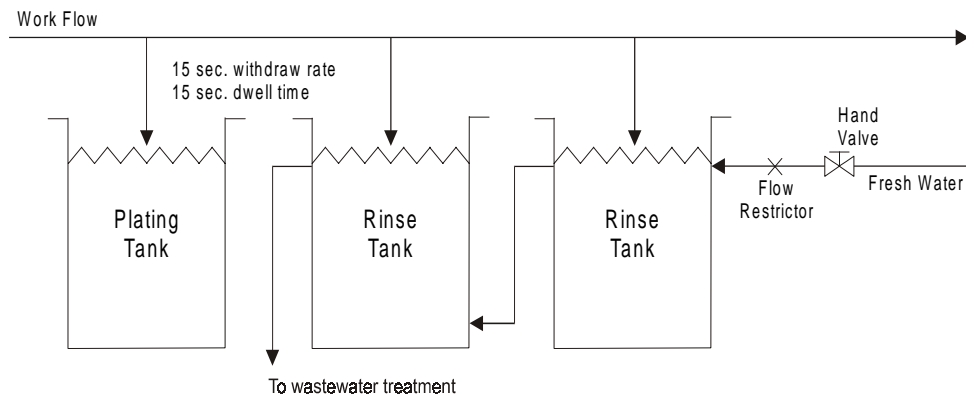


Figure D-1(d). Countercurrent Rinsing with Flow Reduction

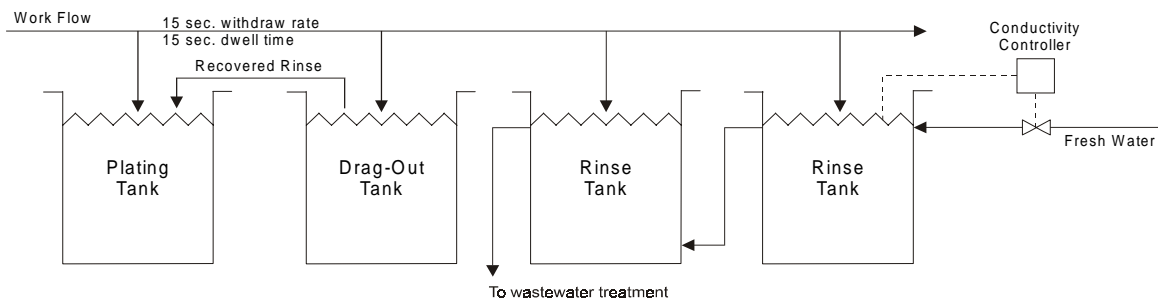


Figure D-1(e). Multiple Rinse Tanks with Flow Reduction and Drag-Out Recovery

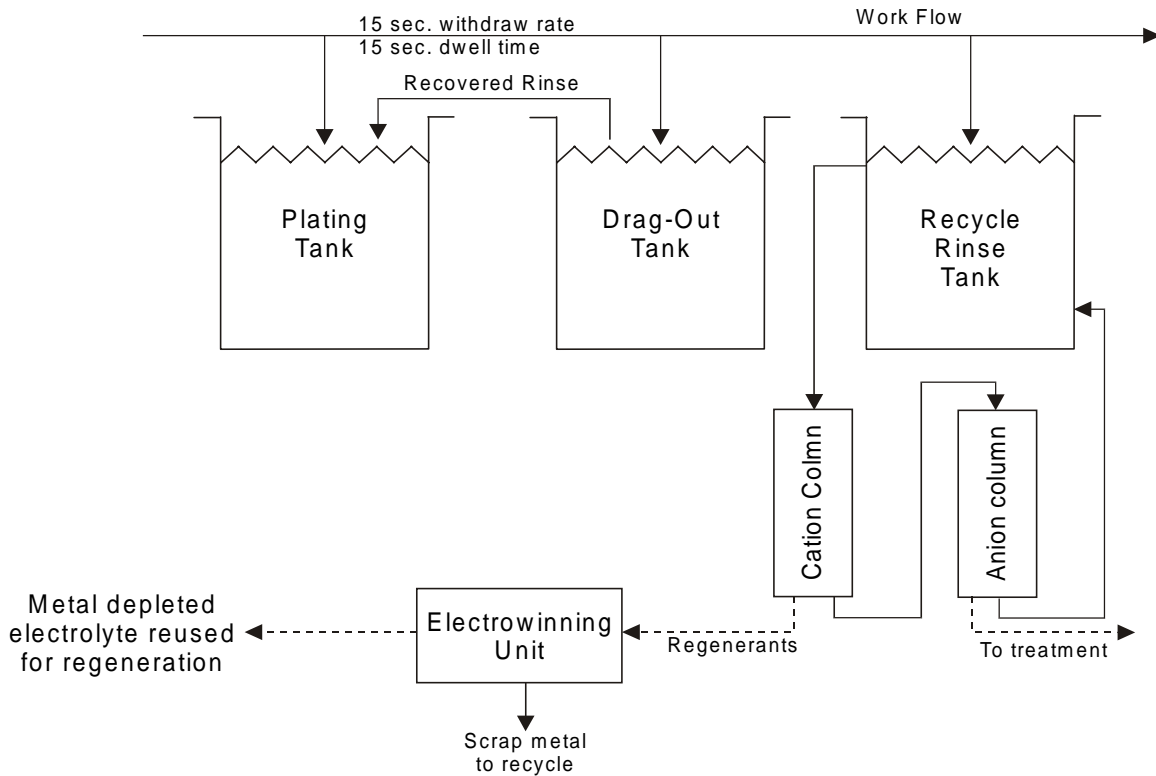


Figure D-1(f). Multiple Rinse Tanks with Water Recycle, Drag-Out Recovery, and Metal Recovery

Figure D-1(a) is an example of inefficient water use. This configuration uses a single-rinse tank with either continuous water flow or manual use control. To coordinate rinse water needs and use, the operator manually turns on the water valve to give the correct flow rate and then turns it off when the flow is no longer needed. The flow-rate setting will usually vary by operator and the water valve may be left open during idle production periods. The single rinse tank configuration uses rinse water at a very high rate, even if water use is coordinated with the introduction of drag-out. In the example shown, with a 1-gallon-per-hour (gph) drag-out rate, the rinse water requirement is 30 gallons per minute (gpm), based on rinsing of Watts nickel plating solution and a rinsing criterion of 50 milligrams per liter (mg/L) nickel. If water use and drag-out introduction are not coordinated, an even higher rinse water use rate would be needed to meet a given rinse criterion.

Figure D-1(b) shows a rinsing configuration where simple rinse water reduction methods have been implemented. The water use is still inefficient because a single rinse tank is used versus multiple rinse tanks. However, with this configuration, the drag-out rate is reduced by controlling the withdrawal rate of the part (increasing the withdrawal rate from 5 to 15 seconds) and by holding the part over the process tank (increasing dwell time from 5 to 15

seconds) to permit the drag-out to drip into the tank. The rinse water flow rate is controlled at a constant flow by a flow restrictor. The flow restrictor is usually sized to provide adequate rinsing at all times, and is more acceptable for constant production rates, such as those often found with automated plating machines. However, this configuration is inefficient when the work is intermittent because the rinse water flow rate must be set high enough to provide adequate rinsing during peak production periods. In addition, a large quantity of rinse water is wasted during low or idle production periods, unless the water flow is manually stopped.

Figure D-1(c) shows a rinsing configuration using multiple rinse tanks, which provides a moderately efficient use of water. This configuration is referred to as parallel rinsing, where each of the two rinse tanks are fed with fresh water and they each discharge to treatment. This arrangement can reduce water use to less than 50 percent of that used in Figure D-1(a).

Figure D-1(d) shows a more efficient rinsing configuration. This configuration is similar to that shown in Figure D-1(c), except that wastewater from the second rinse tank flows back into the first rinse tank to provide more efficient rinsing with less water use. Wastewater from the first rinse tank is then discharged to treatment. In this configuration, known as countercurrent cascade rinsing, the rinse water flows in a direction opposite to the part flow. This arrangement can reduce water use by more than 90 percent over the rinse configuration in Figure D-1(a).

Figure D-1(e) shows a very efficient rinsing configuration. There are three key elements to this rinse system: drag-out reduction/recovery, countercurrent cascade rinsing, and water-use control. This configuration reduces/recovers drag-out by controlling the withdrawal rate and dwell time and by installing a drag-out recovery tank. This tank can reduce the drag-out entering the countercurrent cascade rinses by up to 90 percent, depending on the surface evaporation rate of the process tank. A conductivity controller controls the feed to the countercurrent cascade rinses. This type of device coordinates water use with drag-out introduction and reduces the influence of human error found with manually controlled rinses. An alternative device is a timer rinse control, which is as effective as a conductivity controller when there is no variability in drag-out volume between rinsing events.

Figure D-1(f) shows a rinse system that uses an ion exchange/electrolytic recovery unit as a chemical recovery and water recycling technology. This rinsing configuration can reduce water use by more than 99 percent compared to the rinse configuration in Figure D-1(a), since wastewater is discharged only from the regeneration cycle of the ion-exchange unit.

Table D-1 presents examples of additional practices and technologies that could be components of a well-designed rinse system.

D.1.6 Influences on Flow Rates

Available data show that rinse water use rates are related to production when measured in terms of the surface area of parts processed. Other factors that influence rinse water

use rates include the drag-out rate (gallons per 1,000 square feet of workload), the rinse water purity criteria (mg/L metal), the concentration of TDS in the bath (mg/L TDS), rinse tank design and configuration (e.g., single overflow rinse versus countercurrent cascade rinse), and the type of rinse water flow control (e.g., manual versus conductivity controlled). Section D.1.5 discusses drag-out rinse tank design and configuration and rinse water flow control. The other factors are discussed below.

D.1.6.1 Rinse Water Purity Criteria

Rinse water purity criteria are the levels of tolerable contamination in the rinse water. These levels vary for different processes and types of products. For example, rinse water used after cleaning typically does not have to be as pure as rinse water used following plating, since rinse water that remains on the plated part (essentially the drag-out from the rinse tank) will leave spots after it evaporates if the concentration of dissolved solids in the rinse water is too high. Although preliminary and intermediate processing steps such as cleaning and etching usually do not require as pure a rinse water as final rinsing, the rinse water needs to be pure enough to stop chemical reactions (e.g., etching) and prevent the contamination of subsequent process solutions. Among plating processes, differences also exist in rinse water quality requirements. Parts plated for engineering or functional purposes (e.g., corrosion resistance) can often be rinsed in water that is significantly less pure than decoratively plated parts rinses.

High-purity water is needed for various rinsing operations. In some cases (e.g., electronics parts rinsing), tap water is not pure enough to serve as rinse water. Before use as rinse water for this type of operation, the source water is purified by reverse osmosis and/or ion exchange to remove dissolved solids and other constituents. Source water is sometimes treated even for common rinsing operations, especially when the water supply is high in dissolved solids.

The metal finishing industry has had rinse water quality requirements for decades. They are typically expressed in mg/L of TDS or in conductivity or resistivity units (resistivity is the inverse of conductivity). Table D-8 summarizes some generalized rinse criteria found in the literature (4).

Table D-8**Generalized Rinse Criteria**

| Type of Rinse | Normal Range for Adequate Rinsing (mg/L TDS) |
|---|---|
| Alkaline Treatment/Acid Treatment Rinse | 400 to 1,000 |
| Functional or Engineering Plating Rinse | 100 to 700 |
| Decorative or Bright Plating Rinse | 5 to 40 |

Source: Reference 4.

D.1.6.2 Bath Concentration

The concentration of a bath (which can be expressed in g/L TDS) will affect the quantity of water needed for good rinsing. Baths that are more concentrated (i.e., higher TDS) will require more rinse water to meet the same rinse water purity criteria as a less concentrated bath. The bath concentration depends on the type of bath. For example, a typical acid zinc electroplating bath will have a TDS concentration of 166 g/L and a typical copper cyanide electroplating bath will have a TDS concentration of 250 g/L (6,7). For equal volumes of drag-out from these two baths, the copper cyanide rinse flow must be 1.5 times greater to achieve the same rinse quality criteria (i.e., $250/166 = 1.5$). This calculation does not account for the differences in viscosity that will also affect the volume of drag-out. For example, for flat surfaces, the drag-out rate for a 396-g/L chromic acid bath is 3.8 times greater than that of a 247-g/L bath (6,7). In some cases, the TDS concentration of the bath inadvertently increases due to a buildup of bath contaminants (e.g., iron may accumulate in a chromic acid bath due to the attack of the base metal). The TDS added by the contaminants may affect the drag-out rate in the same manner as its intended bath constituents (e.g., chromic acid). Therefore, operating a bath at the lowest concentration necessary to perform the job properly and maintaining bath contaminants at low levels is a significant pollution prevention measure.

D.1.7 Technical Literature

Table D-9 presents, for several types of rinses, calculated flow rates for a single-stage overflow rinsing configuration and a two-stage countercurrent cascade rinsing configuration. Both rinsing configurations are assumed to have flow control (i.e., water use is coordinated with drag-out introduction using a conductivity control or other device). This table presents the TDS concentration in the associated bath (from literature), the target TDS in the rinse (based on the rinsing criteria), the part type, the assumed drag-out rate, and two production normalized flow (PNF) values.

The first value, PNF 100% Control, is a calculated value based on the assumption that a facility perfectly coordinates work flow and rinse water use (e.g., using a conductivity controller). In actual operations, perfect coordination is nearly impossible to achieve because the quantity of rinse

Table D-9**Rinse Water Required for Various Plating Processes Based on Literature Values**

| Process | Rinse Configuration | TDS Concentration ^a | Target TDS Concentration in Rinse ^a | Part Type | Drag-out Rate ^a | PNF 100% Control (gal/ft ²) | PNF 100%Excess (gal/ft ²) |
|--|--------------------------------|--------------------------------|--|-----------|---|---|---------------------------------------|
| Acid Zinc | Single overflow | 166 g/L | Functional: 100-700 mg/L (used 400 mg/L) | Flat | 1.3 gal/1,000 ft ² | 0.54 | 1.1 |
| | | | | Contoured | 3.5 gal/1,000 ft ² | 1.5 | 2.9 |
| | 2-stage countercurrent cascade | 166 g/L | Functional: 100-700 mg/L (used 400 mg/L) | Flat | 1.3 gal/1,000 ft ² | 0.024 | 0.048 |
| | | | | Contoured | 3.5 gal/1,000 ft ² | 0.072 | 0.14 |
| Silver Cyanide | Single overflow | 370 g/L | Bright: 5-40 mg/L (used 20 mg/L) | Flat | 1.2 gal/1,000 ft ² | 22 | 44 |
| | | | | Contoured | 3.2 gal/1,000 ft ² | 58 | 120 |
| | 2-stage countercurrent cascade | 370 g/L | Bright: 5-40 mg/L (used 20 mg/L) | Flat | 1.2 gal/1,000 ft ² | 0.16 | 0.32 |
| | | | | Contoured | 3.2 gal/1,000 ft ² | 0.43 | 0.87 |
| Copper Cyanide | Single overflow | 250 g/L | Functional: 100-700 mg/L (used 400 mg/L) | Flat | 0.91 gal/1,000 ft ² | 0.57 | 1.1 |
| | | | | Contoured | 3.2 gal/1,000 ft ² | 2 | 4 |
| | 2-stage countercurrent cascade | 250 g/L | Functional: 100-700 mg/L (used 400 mg/L) | Flat | 0.91 gal/1,000 ft ² | 0.023 | 0.046 |
| | | | | Contoured | 3.2 gal/1,000 ft ² | 0.081 | 0.16 |
| Acid Descale | Single Overflow | 248 g/L | Clean: 400-1000 mg/L (used 700 mg/L) | Flat | 1 gal/1,000 ft ² (estimated) | 3.5 | 7.1 |
| | | | | Contoured | 3 gal/1,000 ft ² (estimated) | 11 | 21 |
| | 2-stage countercurrent cascade | 248 g/L | Clean: 400-1000 mg/L (used 700 mg/L) | Flat | 1 gal/1,000 ft ² (estimated) | 0.019 | 0.038 |
| | | | | Contoured | 3 gal/1,000 ft ² (estimated) | 0.056 | 0.11 |
| Alkaline Clean (Proprietary Chemistry) | Single overflow | 90 g/L | Clean: 400-1000 mg/L (used 700 mg/L) | Flat | 1 gal/1,000 ft ² (estimated) | 0.13 | 0.26 |
| | | | | Contoured | 3 gal/1,000 ft ² (estimated) | 0.39 | 0.77 |
| | 2-stage countercurrent cascade | 90 g/L | Clean: 400-1000 mg/L (used 700 mg/L) | Flat | 1 gal/1,000 ft ² (estimated) | 0.011 | 0.022 |
| | | | | Contoured | 3 gal/1,000 ft ² (estimated) | 0.033 | 0.066 |

Sources: References 4, 6, and 7.

^aTDS concentrations are from References 6 and 7, based on bath formulations. Target TDS concentrations are based on criteria presented in Section 3.2.1 (Reference 4). Drag-out rates are from References 4 and 5 unless data were not available, in which case rates were assumed based on technical knowledge of the operations.

Table D-9 (Continued)

1. Acid zinc formulation:

| | |
|--|---------|
| ZnSO ₄ (7H ₂ O) | 240 g/L |
| NH ₄ Cl | 15 g/L |
| Al ₂ (SO ₄) ₃ (18H ₂ O) | 30 g/L |
| Licorice | 1 g/L |

2. Equation used to calculate rinse flow and flow per square foot for single overflow rinse:

Solving for Q:

Where:

| | | |
|----------------|---|--|
| D | = | Drag-out per ft ² (gal) |
| C _e | = | Target concentration of rinse (oz/gal) |
| C _o | = | Concentration of process bath (oz/gal) |
| C _r | = | Target concentration of final rinse (oz/gal) |
| M | = | Interval between drag-out events (minutes) |
| Q | = | Flow (gal/min) |

Note: Any interval M can be chosen. Q, when divided by the work rate, ft²/M, yields the gal/ft² in the table and the gal/ft² number remains the same for any M.

3. Equation used to calculate 100 percent controlled flow and gallons per square foot for countercurrent cascade rinse:

xWhere n = number of rinse stages

For 50 percent controlled flow, Q was multiplied by a factor of 2.

With 100 percent controlled flow, the introduction of drag-out and rinse water into the rinse tank are perfectly coordinated and, therefore, the rinse water required to meet the target concentration of the final rinse is equal to Q. With 100 percent excess flow, the introduction of drag-out and rinse water are not perfectly coordinated and an excess of 100 percent of Q (or 2Q) is used to meet the target concentration of the final rinse.

4. Silver cyanide formulation (middle of high-speed bath range):

| | |
|--------------------------------|-----------|
| AgCN | 97.5 g/L |
| KCN | 152.5 g/L |
| K ₂ CO ₃ | 52.5 g/L |
| KNO ₃ | 50 g/L |
| KOH | 17 g/L |

5. High-efficiency copper cyanide formulation:

| | |
|------|---------|
| CuCN | 75 g/L |
| KCN | 133 g/L |
| KOH | 42 g/L |

6. Acid descale formulation:

| |
|--|
| 20% H ₂ NO ₃ (by volume) |
| 1.5% HF (by volume) |

All bath formulations and equations are from References 4, 6, and 7.

water needed to meet a given rinse criterion usually cannot be added exactly at the time that drag-out enters and is dispersed in the rinse tank. For example, when a barrel of parts is rinsed, it is usually placed in a rinse tank for 1 to 3 minutes. The rinse water volume needed to meet the rinse criterion may be 50 gallons or more. The flow rate of water into the rinse tank is typically less than 10 gpm (flow rates into rinse tanks vary depending on the pipe size and water pressure and may be reduced by a flow restrictor). Therefore, it may take 5 minutes to add the 50 gallons of rinse water. Because of this, actual water use rates will be higher than those presented in the column, PNF 100% Control. A reasonable assumption is that good water flow control will result in a PNF twice that of the calculated values that assume 100 percent control. These flows are shown as PNF 100% Excess.

D.2 Machining Operations

Many machining operations use metal-working fluids to cool and lubricate parts and machining tools during cutting, drilling, milling, and other machining operations. These fluids become contaminated and begin to lose their working characteristics. If neglected, the fluids become unusable and require treatment and disposal. Through proper care, the life span of the fluids can be extended indefinitely. For most machining operations, prolonging metal-working fluid life reduces the cost of treatment and disposal, as well as the cost of fresh coolant.

Many MP&M facilities use some type of pollution prevention and water conservation practices for machining wastewaters. Some facilities have implemented numerous pollution prevention and water conservation methods and technologies that result in very low machining wastewater discharge rates and in some cases eliminate the discharge of machining fluids. Pollution prevention and water conservation practices are applicable to all machining operations; however, process-related factors and site-specific conditions may restrict the utility of certain methods.

D.2.1 Wastewater Generation from Machining Operations

Various types of metal-working fluids, also termed cutting fluids and coolants, are used in machining operations to improve the life and function of machine tools. During machining, these fluids are circulated over working surfaces, reducing friction, cooling the tool and part, and removing metal chips from the work face. The type of fluid used depends on the type of machining being performed and the preference of the site. The fluids are broadly divided into four groups: straight oil (neat oils), synthetic oils, semisynthetic, and soluble oil. The most commonly used fluids are soluble oils, synthetics, and semisynthetics.

Water-soluble coolants are prepared by mixing a concentrated coolant with water in a 1:15 to 1:30 ratio to produce a fluid with a 90- to 98-percent water content. Most water-soluble coolants are suitable for light- and medium-duty operations. Synthetic coolants are designed for high cooling capacity, lubricity, and corrosion prevention. Common chemical agents in synthetics include: amines and nitrites for rust prevention; nitrates for nitrite stabilization; phosphates and borates for water softening; soaps and wetting agents for

lubrication; phosphorus, chlorine, and sulfur compounds for chemical lubrication; glycols to act as blending agents; and biocides to control bacteria growth. Semisynthetics contain small dispersions of oil in an almost otherwise organic water-dilutable system. Straight oils are good lubricants, but are less effective for cooling, and therefore are limited mostly to use in low-speed operations (8).

Metal-working fluids are periodically discarded because of reduced performance or development of a rancid odor. The fluids that contain a large percentage of oil typically are contract hauled as solid waste for disposal or recovery. Fluids with lower oil content typically are sent to a site's wastewater treatment system for treatment and subsequent discharge.

Metal-working fluids degrade mainly because of contamination with tramp oil and dirt and by bacterial growth, which can be accelerated by tramp oil contamination. Tramp oil contamination is caused mostly by oil from the part's surface during machining and by leaks of lubricating and hydraulic oils from the machine. Airborne dust or poor housekeeping practices can cause dirt to accumulate. Bacteria are initially contributed from the surfaces of the machine and parts and from the air. More than 2,000 known species of bacteria have been reported to affect and eventually destroy the stability of machining fluids (9). Bacteria feed on the fluids' chemicals, causing the fluids to lose lubricity and corrosion inhibition. Under anaerobic conditions, sometimes caused by floating tramp oil in coolant sumps, bacteria generate a hydrogen sulfide odor.

In addition to spent fluid, machining operations may generate wastewater from rinsing. Machined parts may be rinsed to remove fluid, chips and other foreign materials. However, parts typically are not rinsed following machining. More frequently, the fluid is permitted to remain on the part to inhibit corrosion, is wiped off using shop towels, or is cleaned in an alkaline cleaning or degreasing operation.

The quantity of wastewater generated by a machining operation depends primarily on the volume of work performed. Production volume can be roughly measured by the quantity of metal stock removed by turning, milling, boring, broaching, cutting and other machining operations. For most machining operations, the removed metal consists of small fragments called chips or fines. Most chips carry a thin film of fluid on their surfaces, which, when it drains, is another source of wastewater.

D.2.2 Pollution Prevention and Water Conservation Practices for Machining Operations

The Agency has identified two categories of pollution prevention and water conservation practices and technologies that can be used to reduce metal-working fluid discharge: those used to prevent metal-working fluid contamination and those used to extend the life of machining fluids, including recovering and recycling metal-working fluids. Within each of these categories are several specific practices and technologies. Table D-10 presents several examples of these practices, which are discussed below. There may be other practices and

technologies not identified here that can reduce metal-working fluid discharge. Therefore, the list provided below is not exhaustive.

Table D-10

**Potential Pollution Prevention and Water Conservation Methods
Applicable to Machining Operations**

| Pollution Prevention/Water Conservation Method | Examples | Applicability |
|--|--|--|
| Prevention of Metal-Working Fluid Contamination | | |
| Reduce contamination from tramp oil | Use coolant in hydraulic and other oil systems. | Applicable to most machines. In most cases, requires use of special fluid. |
| | Replace hydraulics with electrical systems. | Limited applicability. Practical only during major equipment overhaul. |
| | Machine maintenance. | Applicable to all machines. Should be performed at regularly scheduled intervals. |
| Reduce contamination from make-up water | Use deionized water for initial make-up of working fluid and to account for evaporative losses. | Applicable to all machining operations using a water-soluble fluid. Especially important in areas where the water supply is high in TDS. |
| Reduce contamination from sumps | Sterilize sumps during clean-out using steam. | Applicable to all machining operations. Especially important with large concrete sumps. |
| | Use metal inserts or coat walls of concrete sumps. | Applicable to in-ground concrete sumps. |
| Extension of Metal-Working Fluid Life | | |
| Raw material substitution | Use high quality fluids with needed "additive package." | Most machining operations can benefit from the use of high-quality fluids that can extend fluid life, while reducing bacterial growth, improving lubricity, reducing friction, and providing corrosion protection. |
| Equipment modification | Replace sump's air agitation with mechanical agitation. | Applicable to central sumps with air agitation. |
| | Install tramp oil removal device. | Limited mainly to external sumps. |
| Fluid Monitoring | Measure pH, coolant concentration, tramp oil concentration, and bacterial count weekly or more frequently. | Applicable to all machining operations. Larger operations can use data for statistical process control. |

Table D-10 (Continued)

| Pollution Prevention/Water Conservation Method | Examples | Applicability |
|--|--|--|
| Extension of Metal-Working Fluid Life (continued) | | |
| Metal-working fluid recycling | Use methods and technologies for removing fluid contaminants (e.g., filtration, centrifuge, pasteurization). | Simple filtration methods can be used by all machining operations. More sophisticated equipment is limited to larger operations. |
| | Recycle chip drainage. | Applicable to all machining operations. Requires clean handling and storage methods to prevent contamination. |

Source: MP&M Site Visits, MP&M Surveys, Technical Literature.

D.2.2.1 Prevention of Metal-Working Fluid Contamination

Facilities can implement various methods to reduce the amount of fluid contamination. Several of these methods are discussed below.

Reduction of Contamination From Tramp Oil. Tramp oil is a primary contaminant in machining fluids and for many facilities the major cause of metal-working fluid degradation. EPA has identified the following methods to reduce contamination of metal-working fluid with tramp oil.

- Use of Coolant in Hydraulic and Other Oil Systems. Some metal-working coolants are formulated to be used as hydraulic fluid and/or lubricant in concentrated form and as a coolant in its dilute form (i.e., diluted with water). When used as a hydraulic fluid or lubricant, leaks of the fluid will assimilate into the coolant without causing contamination.
- Replacement of Hydraulics with Electrical Systems. Hydraulic systems on some machines can be replaced by newer electrical systems that do not contain hydraulic fluid. This replacement could be economically performed during major equipment overhauls.
- Machine Maintenance. Machine design and age may affect the quantity of hydraulic oil that leaks to the metal-working fluid during machining operations. There are numerous hydraulic systems used with machines, depending on the type of machine. These systems will leak variable quantities of oil depending on design, sealing mechanisms, operating pressures, and other factors. Older machines, especially those that are not properly maintained, can leak excessively from hydraulic seals. Facilities

should implement scheduled maintenance of machines to check and repair sealing mechanisms.

Reduction of Contamination from Make-Up Water. Make-up water contributes to the dissolved solids content of the metal-working fluid, reducing fluid life. This problem occurs more rapidly when water with high TDS is used for evaporative make-up. Certain dissolved solids or minerals cause more problems for metal-working fluids than others. For example, chloride salts and sulfates corrode at levels of greater than 100 parts per million. Sulfates also promote the growth of sulfate-reducing bacteria that cause fluids to become rancid. When minerals become concentrated in the fluid, they can cause increased corrosion, gumming, and machine wear (6). Consequently, using hard water can reduce the fluid life. Deionized (DI) water can be used in place of hard water (DI units can be either purchased or rented).

Reduction of Contamination from Sumps. EPA has identified the following examples of methods to reduce contamination from metal-working fluid sumps:

- Steam Cleaning of Sumps. Machine coolant sumps harbor bacteria that degrade the fluids. If coolant sumps are not sterilized during cleanouts, residual bacteria may degrade the fresh coolant added to cleaned sumps. Steam cleaning the sumps during cleanout can eliminate bacteria.
- Sump Modification. Many coolant sumps are designed as in-ground concrete tanks, whose porous concrete surfaces absorb oil and promote bacterial growth. Improving the design of the sumps can extend fluid life. Potential design changes include inserting metal tanks and coating sump walls with fiberglass or other nonporous material.

Reduce Miscellaneous Contamination. Good housekeeping practices can extend metal-working fluid life by reducing contamination. Facilities can implement housekeeping procedures to keep floor sweepings, solvents, paint chips, soil, rags, paper, and other debris out of the coolant sumps.

D.2.2.2 Extension of Metal-Working Fluid Life

Facilities can implement several methods to extend the life of metal-working fluids. These include raw material substitution, equipment modification, and fluid monitoring, as discussed below.

Raw Material Substitution. As discussed above, four general types of metal-working fluids are used in machining operations. Within a given group of fluids, such as soluble oil, various formulations are used. Within each group, the major difference from one fluid to another is the “additive package.” Additives are included in most metal-working fluid formulations to improve fluid performance (e.g., improve lubricity, reduce friction, or increase corrosion protection) and increase life span (e.g., reduce bacterial growth). Costs of different

metal-working fluids can vary by 100 percent or more. Fluids with additive packages that do not meet the lubrication and cooling requirements of the specific machining operation may degrade faster than other metal-working fluids. These fluids will need to be replaced more often and increase overall operating costs. These fluids may also affect tool life, further increasing operating costs. Therefore, using the proper grade metal-working fluids can increase the life span of the fluid, reducing the generation of waste machining fluids and decreasing the overall operating costs.

Equipment Modification. EPA has identified the following examples of equipment modifications that can extend the life of machining fluids.

- Replacement of Air Agitation With Mechanical Agitation. Some facilities use air agitation in central coolant sumps to constantly mix the fluid and prevent phase separation and pooling of tramp oil. However, air agitation increases the activity of aerobic bacteria by adding oxygen, which causes the bacteria to consume fluid additives. An alternative method of mixing is mechanical agitation (i.e., pumping). Mechanical agitation mixes without increasing the oxygen concentration of the coolant.
- Removal of Tramp Oil. Machining fluid life can be extended by continuous, in-sump removal of tramp oil. Facilities can install continuous oil-skimming devices directly in the machine sump to remove tramp oil. Absorbent blankets, fabrics, or pillows can also remove tramp oil.

Fluid Monitoring. During use, the metal-working fluid undergoes various physical, chemical, and biological changes. If the properties of the fluid are monitored on a regular basis, the fluid can be adjusted before it is degraded. Parameters measured to monitor the fluid include: pH, coolant concentration (using a refractometer or titration kit), TDS, tramp oil (visual) and biological activity (using dip slides available from coolant suppliers and laboratories (6) or other methods). Facilities can use these data to guide periodic fluid adjustments and/or develop statistical process control (SPC) procedures. Facilities may wish to monitor fluid concentration at least weekly, if not daily, to identify contamination. The correct pH operating range of most coolants is 8.5 to 9.5. If the pH drops below the operating range, coolants may cause rusting and be prone to increased biological activity. Dilute concentrations can shorten tool life, increase biological activity, and cause rust. Rich concentrations can lead to foaming and tramp oil contributes to biological growth.

D.2.2.3 Metal-Working Fluid Recycling

Most metal-working fluids can be recycled on-site by removing contaminants accumulated during use and storage. Recycling methods include settling, straining, skimming, simple filtration, membrane filtration, coalescing, centrifugation, cyclone separation, magnetic separation, and pasteurization. Some of these methods can be used in combination to recover

nearly 100 percent of the metal-working fluid. Facilities can purchase recycling equipment or hire commercial services that perform on-site processing (10,11,12). A self-contained recycling unit can be purchased that is specifically designed for smaller machine shops and is a complete sump maintenance and fluid recycling system in one unit (8). In most cases, facilities can facilitate metal-working fluid recycling by consolidating the types of machining fluids they use to one or two types of fluid.

Additional metal-working fluid can be recycled by chip drainage. Chip drainage can account for up to 50 percent of annual fluid use (11). During machining, the metal chips (scraps) become coated with fluid. Part of the fluid drains from the chips and part remains on the chips. In many cases, the chips and associated fluid drop to the floor and are manually collected in storage containers. Some machines send the chips and fluid to a storage container using automated equipment (e.g., belt or pneumatic conveyor). Fluid that drains from chips can be recycled rather than discharged, which may require design changes of chip handling and storage equipment.

D.2.2.4 Design of the Machine Fluid System

Fluids used in machining are stored either in sumps dedicated to individual machines (either internal or external to the machine), or in central sumps that serve multiple machines. Large machining operations typically use central sumps, whereas small machine shops tend to have individual sumps for each machine. Central systems usually contain three to five times greater volume of fluid per machine from individual sumps. The reservoir volumes of most machines with internal sumps are typically 10 to 50 gallons. External sumps serving a single machine typically have a volume of 1,000 to 2,500 gallons. Central sumps may have volumes that exceed 50,000 gallons.

The amount of make-up fluid in a central system amounts to a smaller percentage of total fluid than in a single machine operation. Consequently, the potential for bacterial degeneration is greater in central systems as the bacteria have a longer time in which to degrade the fluid (9). Further, central sumps are often unlined concrete basins, whose porous walls harbor bacteria and prevent complete disinfecting during cleanouts. This reduces the time needed for the bacteria to become reestablished (11). Additionally, the larger pumps used in central systems keep the tramp oils suspended in the fluid so they do not readily “float out,” adding to further bacterial attack. Central systems may require more maintenance than dedicated sumps to prevent bacterial growth.

D.2.2.5 Machining Operations Performed

The ratio of scrap metal (e.g., chips) generated to fluid used varies among machining operations. For example, metal cutting may generate large pieces of scrap metal using a small volume of fluid, whereas a milling operation usually produces a much smaller mass of chips for the same volume of fluid.

D.2.2.6 Base Material Being Machined

The type of base material being machined affects the quantity of metal-working fluid used. The hardness of base materials varies, which in turn affects the speed at which the base metal can be removed. Harder metals require more fluid than softer metals for the same operation.

D.2.2.7 Climatic Conditions

The temperature of the shop can affect the life span of metal-working fluid in that warmer temperatures may foster the growth of certain bacteria.

D.2.2.8 Design and Age of Machines

The design and age of machines may affect the quantity of hydraulic oil that is leaked to the metal-working fluid during machining operations. Numerous hydraulic systems are used with machines. These systems will leak variable amounts of oil depending on design, sealing mechanisms, operating pressures, and other factors. Older machines, especially those that are not properly maintained, can have hydraulic seals that excessively leak.

D.2.2.9 Uniform Coolant Use

Minimizing the number of different machine coolants used at a facility reduces the chance of formulation errors. When employees are familiar with fluid properties and coolant formulation chemistry, it is less likely that coolant batches will be prepared incorrectly, which many times requires the entire batch to be discharged to the on-site wastewater treatment facility. Facilities may also save money by purchasing larger volumes of coolant (i.e., economies of scale).

D.3 Painting Operations

Paint is applied to a base material for protective and decorative reasons in various forms, including dry powder, solvent-diluted formulations, and water-borne formulations. There are various methods of application, the most common being immersion and spraying. Water is used in painting operations in paint booth water-wash systems (water curtains), in water-borne formulations, in electrophoretic painting solutions and rinses, and in clean-up operations. This discussion is directed at water use in spray painting booths; however, this subsection also provides some information on rinsing following electrophoretic painting and water clean-up.

D.3.1 Wastewater Generation from Painting Operations

In spray painting, an organic coating is applied to a product. During manufacturing operations, spray painting is usually performed in a booth to control the introduction of contaminants and the release of solvent and paint to the work place and

environment, and to reduce the likelihood of explosions and fires. Paint booths are categorized into two types (dry filter or water wash) and by the method of collecting the overspray (i.e., the paint that misses the product during application). The type of booth design selected depends mainly on production requirements, including part size and configuration, production rate and transfer efficiency, the material being sprayed, and finish quality requirements.

Dry-filter booths use filters to screen out the paint solids, by pulling prefiltered air through the booth, past the spraying operation, and through the filter. The air entrains the overspray and is pulled through the filter, which collects the paint. Solvent evaporates from the paint, leaving the paint solids on the filter. Filters are periodically replaced when they become laden with paint solids and the air flow through them is restricted. Dry-filter booths are most often used when paint usage does not exceed 20 gallons/8-hour shift/10 feet of chamber width (13). At higher usage rates, the frequency of filter changes greatly increases operating costs (i.e., filter, filter disposal, cost, and labor).

The only water used with dry filter units is to clean painting equipment (e.g., guns and lines) when water-borne paints are used. The operation of dry-filter units is essentially dry when solvent-based paints are used.

Water-wash booths use a “water curtain” to capture paint overspray. Air containing entrained paint overspray is pulled through a circulating water stream, which “scrubs” the overspray from the air. There are two primary types of water-wash booths, side-draft and downward-draft. The basic difference between the two types is the way the air moves through the system to draw the paint overspray in for capture (14,15). Small operations typically use side-draft units and large and/or continuous operations use downward-draft units.

Water-wash booths use a water stream that recirculates from a sump or tank with a typical capacity of 200 to 5,000 gallons or more. Downward-draft systems normally contain much larger volumes of water than side-draft systems. Water is periodically added to the system as make-up for evaporative losses. The sump water is periodically discharged, usually during general system cleaning or maintenance. The discharge rate depends on various factors, including booth design, paint type, overspray rate, and the water treatment methods used. Water is also used to clean the painting equipment and the paint booth. Booth cleanup may involve using paint stripper to remove dried paint from the walls of the booth and the piping system.

A common practice in water-wash booth operation is to immediately detacify suspended paint solids to reduce maintenance problems and to subsequently separate and remove the solids from the water. The organic resins that make up the bulk of the paint coating are insoluble in water and tend to stay tacky if not treated with some other material added to the water (14,15). If left untreated, the tacky solids can plug recirculation pipes and pumps and adhere to wetted surfaces of the booth. Dissolved solids are either immediately precipitated and flocculated, removed by water treatment, or discarded when the sump is discharged.

Solids can be detacified and removed in various ways, depending on the type of paint used and the booth design. Detacification chemicals include sodium hydroxide (caustic), metal salts, clay, and polymers. Depending on the type of paint and the detacification chemical, the paint solids may either disperse or agglomerate. Agglomerated solids may either sink or float. In solids dispersal, the suspended solids increase in concentration as overspray enters the water. Subsequently, another chemical is added to the water that causes the dispersed solids to agglomerate into a dense floc, which is then removed.

There are various ways to remove paint solids from the booth water-wash system. These removal technologies vary in sophistication, automation, efficiency (removal and separation), and capital and operating costs. The most common methods include passive settling, skimming, screening, filtration (bag, roll bed, press), and centrifugal methods (hydrocyclone, centrifuge).

Besides spray painting, another common method of painting is electrophoretic painting (also known as electrocoating or electrodeposition), which is the process of coating a work piece by making it either anodic or cathodic in a bath that is generally an aqueous emulsion of the coating material. The electrophoretic painting bath contains stabilized resin, pigment, surfactants, and sometimes organic solvents in water. Electrophoretic painting is used primarily for primer coats (e.g., bodies for motor vehicles or mobile industrial equipment) because it gives a fairly thick, highly uniform, corrosion-resistant coating in relatively little time. During this process, precleaned parts carrying an electrical charge are immersed into the coating tank (paint) and then through a rinsing system. Rinsing removes excess paint (drag-out) from the parts. The typical rinsing procedure is a three-stage countercurrent cascade rinse, and may include both dip and spray rinsing. Typically, the final rinse is performed with deionized water.

Ultrafiltration is commonly used to separate and recover paint solids and recycle rinse water, by counter flowing the rinse water into the painting bath and running the bath through the ultrafilter. The ultrafilter removes excess water from the bath, recycles the paint solids to the bath, and recycles the water (permeate) to the rinse system. Occasional blowdown of rinse water is needed to purge the system of contaminants. Processing the rinse water through a reverse osmosis unit can reduce the volume of wastewater discharged (16).

D.3.2 Pollution Prevention and Water Conservation Practices for Painting Operations

EPA has identified three categories of pollution prevention and water conservation practices that, if implemented, can reduce or eliminate wastewater discharges from painting operations: practices to reduce the quantity of paint entering the water system; recycling technologies for paint booth water; and conversion of water-wash booths to dry-filter booths. These are discussed in this subsection and summarized in Table D-11. It is possible, however, that facilities can reduce or eliminate wastewater discharges using different practices than those described here.

Table D-11

**Potential Pollution Prevention and Water Conservation Methods
Applicable to Painting Operations**

| Pollution Prevention/Water Conservation Method | Examples | Applicability |
|---|--|--|
| Reduce the Quantity of Paint Entering the Water System | | |
| Improve spray painting operating practices | Provide operator training to improve racking and positioning of parts to reduce overspray, assure proper selection of nozzle for efficient spray pattern, improve work scheduling and reduce clean-outs, improve housekeeping. | Applicable to all spray painting operations. |
| Improve paint transfer efficiency | Replace inefficient conventional compressed air spray equipment with high-velocity/low-pressure equipment. | Applicable to most existing spray painting operations using conventional equipment. Will require some retraining of operators. |
| Install gun cleaning station | Use gun-cleaning station to clean guns and lines. Can prevent spraying of cleaning fluid/paint into booth. | Applicable to most solvent-based painting operations. |
| Recycle Paint Booth Water | | |
| Recycle paint booth water through solids removal | Use booth water maintenance system that removes paint solids. Applicable technologies include weirs, filters, and centrifuges. | Applicable to most water-wash booths. Usually requires treatment of booth water with chemicals to produce solids that can be separated from water. |
| Use Dry-Filter Booths | | |
| Use dry-filter booths instead of water-wash booths | Convert existing water-wash booth to a dry-filter booth. | Applicable to booths with low to moderate paint usage. In cases of high paint usage, dry filters clog too quickly. |

Source: MP&M Site Visits, MP&M Surveys, Technical Literature.

D.3.2.1 Reducing the Quantity of Paint Entering the Water System

Facilities can implement various methods to reduce the quantity of paint entering the water system. Three of these methods are discussed below.

Improving Spray Painting Operating Practices. Facilities can implement various practices that reduce the quantity of paint and other material entering the water system of a paint booth and thereby reduce the need to discharge wastewater. Generally, implementing these practices requires only operator training. These practices include: racking and positioning parts to minimize overspray; selecting the proper nozzle for an efficient spray pattern; scheduling work to reduce color changes and associated clean-outs of guns, lines, and pots; and housekeeping to prevent painting wastes and foreign materials from entering the booth's water system.

Improving Transfer Efficiency. The transfer efficiency (i.e., spray efficiency) is the amount of coating that is applied to the part divided by the amount of coating that is sprayed from the gun. It is reported as a percentage. The transfer efficiency depends on several factors, including the spraying equipment, part size and configuration, paint type, and operating methods. Improving the transfer efficiency can reduce booth water processing requirements.

During the past 15 to 20 years, spraying equipment has improved, primarily in response to more stringent air pollution regulations and rising paint costs. One of the key improvements has been replacement of conventional compressed air spray equipment by more efficient equipment. In terms of transfer efficiency, the common types of spray equipment are ranked as follows (shown in order of increasing efficiency with relative transfer efficiencies shown in parenthesis): conventional compressed air (25 percent), airless (35 percent), air assisted airless (45 percent), electrostatic, (65 percent), and high-volume/low-pressure (HVLP) (80 percent) (17). The HVLP equipment has been widely implemented due to the high transfer efficiency, as well as the low cost of converting from conventional compressed air equipment. The cost is primarily for the spray guns, since the compressors and other equipment are the same as for conventional compressed air painting equipment.

Installing Gun Cleaning Station. After use, spray-painting equipment must be cleaned to prevent a buildup of paint solids. Spray guns are often cleaned by spraying solvent through the lines and guns and into the booth. However, this practice increases the amount of paint entering the booth's water system and increases emissions of volatile organic compounds (VOCs). An alternative practice is to install gun-cleaning stations. A commercial gun-cleaning unit is designed to sit on top of a 55-gallon drum. The gun is connected to the solvent tank and the drum. Solvent is drawn through the gun and exits into the drum, where it can be recovered by distillation (18).

D.3.2.2 Booth Water Recycle

Various methods and equipment can reduce or eliminate the discharge of the water used in water-wash booths. These methods and equipment prevent the continuous

discharge of booth waters by conditioning (i.e., adding detacifiers and paint-dispersing polymers) and removing paint solids. The least efficient paint booth water-wash system, in terms of water use, is one where the paint solids are not conditioned and accumulate until booth water must be replaced. Cleaning such systems typically involves draining or pumping the water from the booth reservoir and contract hauling the entire waste product. Due to high operating costs and downtime, this procedure is usually used only by low-production operations. Moderate- and high-production operations need daily, if not continuous, booth water maintenance to conserve water. The most basic form of booth water maintenance is removing paint solids by manual skimming and/or raking. These solids can be removed without water conditioning since some portion of solvent-based paints usually floats and/or sinks. With the use of detacifiers and paint-dispersing polymer treatments, facilities can implement more advanced methods of solids removal. Some common methods are discussed below.

Wet-Vacuum Filtration. Wet-vacuum filtration units consist of an industrial wet-vacuum head on a steel drum containing a filter bag. The unit vacuums paint sludge from the booth. The solids are filtered by the bag and the water is returned to the booth. Large vacuum units are also commercially available that can be moved from booth to booth by forklift or permanently installed near a large booth.

Tank-Side Weir. A weir attached to the side of a side-draft booth tank allows floating material to overflow from the booth and be pumped to a filtering tank for dewatering (14,15).

Consolidator. A consolidator is a separate tank into which booth water is pumped. The water is then conditioned by adding chemicals. Detacified paint floats to the surface of the tank, where it is skimmed by a continuously moving blade. The clean water is recycled to the booth (14,15).

Filtration. Various types of filtration units are used to remove paint solids from booth water. The booth water is pumped to the unit where the solids are separated, and the water is returned to the booth. The simplest filtration unit consists of a gravity filter bed with paper or cloth media. Vacuum filters are also used, some of which require precoating with diatomaceous earth (14,15).

Centrifuge Methods. Two common types of centrifugal separators are the hydrocyclone and the centrifuge. The hydrocyclone is used to concentrate solids. The paint booth water enters a cone-shaped unit under pressure and spins around the inside surface. The spinning increases the gravity, which causes most of the solid particles to be pulled outward to the walls of the cone. Treated water exits the top of the unit and the solids exit the bottom. Some systems have secondary filtration devices to further process the solids. The centrifuge works in a similar manner, except that the booth water enters a spinning drum, which imparts the centrifugal force needed to separate the water and solids. Efficient centrifugation requires close control of the booth water chemistry to assure a uniform feed. Also, auxiliary equipment such as booth water agitation equipment may be needed.

D.3.2.3 Conversion of Water-Wash Booths to Dry-Filter Booths

Water-wash booths can be converted to or replaced by dry-filter booths. The dry-filter booths have the potential to eliminate the wastewater discharge, but they create a solid wastestream. The choice between using a water-wash booth or a dry-filter booth is primarily based on the amount of overspray. It is usually cost-effective to use a dry-filter booth when paint usage does not exceed 20 gallons/8-hour shift/10 feet of chamber width (13).

A 1989 U.S. Navy study concluded that conversion from wet to dry booths can be cost-effective for a range of operations. This study included a survey of military and industrial facilities that have successfully converted and an economic analysis based on typical Navy painting operational parameters (1).

D.3.3 Solvent, Paint Solids, and Other Components of Paint

The chemical make-up of the paint can impact wastewater generation. The recirculated water in a water-wash booth contains the various constituents of the paint(s) being applied. With most solvent formulations, the solvents (e.g., xylene, toluene, methylene chloride) are not water-soluble, but can be water-miscible. Some exceptions, such as acetone and methyl ethyl ketone (MEK), are water-soluble. However, in most cases, the solvents are volatile and evaporate over time and exit the booth through the air exhaust system. The organic resins that make up the bulk of the paint coating are insoluble in water and tend to stay tacky if not treated with some additional material introduced to the water (14,15). If left untreated, the tacky solids can plug recirculation pipes and pumps and adhere to wetted surfaces of the booth. Other paint additives, such as wetting agents, pigments, and heavy metals (e.g., zinc and chromium salts) may be soluble in water. These constituents can be made partly insoluble and removed by adjusting the chemistry of the water.

Water-based paints present two problems with regard to water use. First, these paints disperse in water rather than agglomerate like solvent-based paints, making the maintenance of paint booth waters more difficult (14,15). Second, water is used to clean spraying equipment when water-based paints are applied, which may generate wastewater. A typical equipment-cleaning procedure is to flush with water, then solvent, then water (2).

D.3.4 Paint Booth Maintenance Requirements

Water-wash paint booths are periodically shut down for maintenance, which usually involves removing the water in the booth. Various conditions can exist that may necessitate discharging the water, including odor, bacterial growth, foaming, TDS buildup, and the presence of corrosion and scale constituents.

Booth maintenance typically involves incidental repairs and cleaning the booth surfaces and piping system. Often facilities do maintenance according to a schedule, but periodic repairs may also necessitate an unplanned shut-down and clean-out. A common clean-out

procedure is to remove the accumulated paint solids from the water, transfer the water to a holding tank, and return the water after the maintenance is completed. Alternate methods are draining the booth water to a sewer or wastewater treatment system or having it hauled to a disposal site. Systems with accumulated paint solids on the wetted surfaces of the booth and in the piping system can be cleaned by circulating an alkaline cleaner or other chemical for dissolving paint. Since the amount of water discharged from water-wash paint booths is a function of the system's maintenance requirements, newer systems that require less maintenance will discharge less water. Therefore, one pollution prevention option for water-wash paint booths is to install new systems or upgrade existing systems to limit maintenance requirements.

D.4 Cleaning Operations

Cleaning operations include aqueous degreasing, acid treatment, alkaline treatment, and electrolytic cleaning. Depending on the chemicals, equipment, and procedures used, these processes are commonly referred to as immersion, spray, or electrolytic alkaline cleaning; immersion, spray, or electrolytic acid cleaning or pickling; ultrasonic cleaning; and emulsion cleaning and parts washing.

Many MP&M facilities implement pollution prevention and water conservation methods and technologies that result in low cleaning wastewater discharge rates, and in some cases, eliminate the discharge of cleaning solutions. Pollution prevention and water conservation practices are applicable to all cleaning operations; however, process-related factors and site-specific conditions may restrict the utility of certain methods. This subsection identifies pollution prevention and water conservation practices and technologies applicable to cleaning operations.

D.4.1 Wastewater Generation From Cleaning Operations

MP&M facilities commonly perform cleaning as a stand-alone operation or in combination with other proposed MP&M operations such as anodizing, electroplating, conversion coating, and painting. Cleaning removes surface contaminants that affect the appearance of parts or the ability to further process the parts. Various types of acidic and alkaline solutions are used for cleaning.

Alkaline cleaners are usually impacted by organic pollutants such as oil and grease. The effectiveness of most alkaline cleaners is reduced when the oil concentration of the bath is in the range of 1 to 5 g/L or more. Oil and grease enters the alkaline cleaning bath on the parts being processed. The rate of oil buildup depends on the production rate (measured in square feet per day) and the quantity and characteristics of the contamination on the parts. Acid treatment solutions and, to a lesser extent, alkaline treatment solutions accumulate dissolved metals from corrosion of the base metals being processed. The dissolved metal reduces the strength of the cleaning bath. As dissolved metal increases, additional acid or alkaline solution is added; however, at certain metal concentrations, the bath is no longer usable. The tolerable concentration of dissolved metals depends mostly on the type of acid or alkaline solution and the

function of the bath. The buildup rate of dissolved metal depends primarily on the production rate, type and concentration of acid or alkaline solution, type of base metal, duration of cleaning cycle, and bath temperature.

D.4.2 Pollution Prevention and Water Conservation Practices for Cleaning Operations

EPA identified three categories of pollution prevention and water conservation practices that, if implemented, can reduce or eliminate wastewater discharges from cleaning operations: housekeeping and maintenance, oil and suspended solids removal, and dissolved solids removal. These are discussed in this subsection and summarized in Table D-12. It is possible, however, that facilities can reduce or eliminate wastewater discharges using different practices than those described here.

Table D-12

Potential Pollution Prevention and Water Conservation Methods Applicable to Cleaning Operations

| Pollution Prevention/Water Conservation Method | Examples | Applicability |
|---|---|--|
| Housekeeping and maintenance | Check the accuracy of temperature controls; remove sludge build-up from tanks, heat coils and temperature regulators; retrieve parts, racks, etc. dropped into the tanks; and check the integrity of tanks and tank liners. | Applicable to all cleaning operations. |
| Oil and suspended solids removal | Technologies used to remove oil and suspended solids from cleaning solutions, thereby extending the useful life span of the solutions (e.g., skimmers, coalescers, cartridge and membrane filters). | Suspended solids removal equipment (e.g., cartridge filters) are applicable to nearly all baths. The other types of equipment are applicable to most or all alkaline cleaning baths. |
| Dissolved solids removal | Various technologies and processes that remove dissolved metals from baths, including acid sorption, diffusion dialysis, and membrane electrolysis. | Applicable to acid and alkaline solutions that become contaminated with dissolved metal, usually due to etching of the basis metal. |

Source: MP&M Site Visits, MP&M Surveys, Technical Literature.

D.4.2.1 Housekeeping and Maintenance

Facilities can implement various housekeeping and maintenance practices to reduce the quantity of cleaning solution discharge. Several of these practices are discussed below.

Solution Testing. The chemical make-up of cleaning solutions changes over time due to evaporative losses, water additions, cleaning chemical drag-out, chemical reactions, and drag-in of impurities. Because of these factors, cleaning baths lose strength, performance declines, and solutions require disposal. Many facilities operate cleaning baths on a three-step schedule: formulate, use, and discard. This procedure can be expensive and inefficient from a production standpoint, and generates large volumes of wastewater. For this reason, facilities should frequently test the strength of the cleaning solution and appropriate chemical additions needed to continue using the solution. By implementing testing and recordkeeping, facilities can reduce the disposal frequency of cleaning baths.

Most alkaline cleaning solutions are proprietary formulations, and the vendors of these solutions provide test methods for determining the condition of a bath. Also, commercial test kits are available that include generic test methods. For example, the strength of an alkaline cleaning solution can be tested using acid-base titration, which measures alkalinity. Also, there is a dual test method that indirectly measures the level of contamination in the cleaner. This process consists of titrating a measured sample of cleaner (e.g., 5 milliliters (ml)) and then adding a color indicator (phenolphthalein or methyl orange) with an acid of precise concentration (e.g., 1N solution of sulfuric acid). Phenolphthalein is used as the indicator to measure free alkalinity and methyl orange is used to measure total alkalinity. By performing both tests, the ratio of total alkalinity to free alkalinity can be calculated. A ratio close to 1 indicates that the cleaner is relatively free of contamination, while a higher ratio indicates that contamination exists. Facilities sometime use this ratio to determine if they should discharge a cleaning solution. For example, a common guideline used is that the solution is discarded when the ratio exceeds 2.0. The total alkalinity/free alkalinity test method does not work for all cleaners. Because of additives used, some alkaline cleaners do not have any free alkalinity. In such cases, the facility may want to perform more detailed tests to accurately determine the contaminant concentration (e.g., oil and grease measurement).

Similar test methods exist for acid cleaners. The most common parameters in acid cleaner test programs are acid concentration and dissolved metal concentration. The concentration of sulfuric acid or hydrochloric acid in pickling solutions is usually measured by titrating a sample of the solution with sodium carbonate and using a methyl orange indicator. Iron and other dissolved metals can also be measured by titration or by using laboratory analytical equipment such as an atomic adsorption spectrophotometer.

Recordkeeping. Maintaining accurate records of bath additive rates and bath lives can help facilities identify trends in solution use and focus on extending the lives of those that are

frequently discarded. Important records to keep are occurrences of chemical additions and solution dumps, production throughput, and chemical concentration data.

Miscellaneous Housekeeping and Maintenance. To obtain consistently good cleaning results and reduce their solution discharge, facilities should implement a regular schedule of housekeeping and maintenance. Tasks should include: checking the accuracy of temperature controls; removing sludge buildup from tanks, heating coils, and temperature regulators; retrieving parts, racks, and other foreign materials dropped into the tanks; and checking the integrity of tanks and tank liners.

D.4.2.2 Oil and Suspended Solids Removal

Cleaning baths accumulate oil and suspended solids during use. These contaminants eventually reach a concentration that interferes with the effectiveness of the cleaning process, despite the fact that most bath constituents remain usable. Also, contaminated cleaning baths may carry over contaminants to subsequent process solutions. As a result, cleaning baths are often discarded when they reach a certain concentration of contaminants. There are several technologies used to remove oil and suspended solids from cleaning solutions, thereby extending the useful life of the solutions. These technologies are primarily applicable to alkaline cleaning baths and are discussed below.

Free/Floating Oil Separation Devices. Separation devices for oil/water mixtures use the difference in specific gravity between oils and water to remove free or floating oil from wastewater. Common separation devices for cleaning solutions include skimming devices (disks, belts, and rotating drum oil skimmers) and coalescers. These devices are not suited for emulsified oil removal, which typically is addressed through chemical treatment or membrane filtration.

Skimming is a simple method of separating floating oil from cleaning solutions. Skimming devices are typically mounted onto the side of a tank and operate on a continuous basis. The disk skimmer is a vertically rotating disk (typically 12 to 24 inches in diameter) that is partially submerged into the liquid of a tank (typically 4 to 12 inches below the surface). The disk continuously revolves between spring-loaded wiper blades that are located above the surface. The adhesive characteristics of the floating oil cause it to adhere to the disk. As the disk surface passes through the wiper blades, the oil is removed and diverted to a run-off spout for collection. Maximum skimming rates typically range from 2 to 10 gallons per hour of oil. Belt and drum skimmers operate similarly, with either a continuous belt or drum rotating partially submerged in a tank. As the surface of the belt or drum emerges from the liquid, the oil that adheres to its surface is scraped (drum) or squeezed off (belt) and diverted to a collection vessel.

Coalescers separate liquids with specific gravity differences of 0.09 and greater. Coalescers are typically tanks containing a coalescing media that accelerates phase separation (3). A suction skimmer removes cleaning solution and oil from the process tank and pumps it to the coalescer. The media in the coalescers is a material such as polypropylene, ceramic, or glass

that attracts oil in preference to water (i.e., oleophilic). The oil/cleaner mixture passes through the unit and the oil adheres to the coalescing media. The oil forms droplets that conglomerate and rise to the surface of the tank, where a skimming device or weir removes them. According to Stoke's Law, the rise/fall velocity of a dispersed-phase droplet is exponentially increased with the droplet size. Therefore, the coalescing media separates the phases more rapidly than a common gravity settling device.

Media Filtration Methods. Filtration removes suspended solids from cleaning solutions. Common types of filters include cartridge filters, precoat diatomaceous earth filters, and sand or multimedia filters. Cartridge filters are available with either in-tank or external configurations; the in-tank filters typically are used for small tanks and the external filters for larger tanks. Most cartridges are disposable; however, washable and reusable filters are available, which further reduce waste generation. Precoat, sand, and multimedia filters are used mostly for large tank applications. The type of filter media used is based on the chemical composition of the bath. All filtration systems are sized based on solids loading and the required flow rate. Typical flow rates for cleaning solution applications are two to three bath turnovers per hour.

Membrane Filtration. Microfiltration and ultrafiltration are membrane-based technologies used primarily to remove emulsified oil and other colloids from cleaning solutions. The solution entering a microfiltration or ultrafiltration unit typically is prefiltered using media filters to remove large particulates. Various devices then trap or skim floating oils and allow heavier solids to settle. The solution is pumped into the membrane compartment, where the membrane traps remaining oil and grease while water, solvent and other cleaning bath constituents pass through. The fluid flows parallel to the membrane with enough velocity to remove the reject from the membrane surface. Ceramic membranes are available in various pore sizes ranging from several hundred angstroms to over 0.2 microns. The appropriate pore size is determined by the specific cleaner to be filtered. The capacity of a unit is based on the total area and flux rate of the membrane. Commercially available units range in capacity from less than 260 to more than 1,300 gallons per day.

D.4.2.3 Dissolved Metals Removal

Metals become dissolved in acid and alkaline cleaning solutions as a result of corrosion of the base metal. The dissolved metal forms salts or other compounds that reduce the strength of the cleaning bath. Technologies used to remove dissolved metals include acid sorption, diffusion dialysis, and membrane electrolysis, discussed below.

Acid Sorption. Acid sorption is an acid purification technology that is applicable to various acid treatment solutions, as well as other acidic baths (e.g., anodizing baths). The acid sorption unit resembles an ion-exchange column. The column contains a bed of alkaline anion exchange resin that separates the acid from the metal ions.

First, spent acid is pumped upward through the resin; the acid is absorbed by the resin while the metal ions pass through it. The resulting metal-rich, mildly acidic solution is collected at the top of the bed. Water is then pumped downward through the bed and desorbs the acid from the resin. The purified acid solution is collected at the bottom of the bed. This technology can recover approximately 80 percent of the free acid remaining in a spent acid treatment solution. Purification can be performed in a batch mode, but is most effective in a continuous flow mode (usually expressed in terms of the mass of metal removed from the acid solution per unit of time). Equipment capacity ranges from 100 grams/hour to several thousand grams/hour. Units are sized to remove metal near or above the rate at which the metal is being introduced. Typically, a facility determines a target level of metal concentration and sizes the unit to maintain that level.

Diffusion Dialysis. Diffusion dialysis is a membrane process that separates metal contaminants from the acid solution using an acid concentration gradient between solution compartments. Anion exchange membranes makeup the compartments. The membranes are usually assembled in a membrane stack, like that used with electrodialysis. The contaminated acid passes through one set of compartments and deionized water through the adjacent compartments. Acid is diffused across the membrane into the deionized water whereas metals are blocked due to their charge and the selectivity of the membrane. Unlike electrodialysis, this process uses no electrical potential. The acid diffuses because of the difference in acid concentration on either side of the membrane (i.e., material in high concentration moves to an area of low concentration).

Membrane Electrolysis. Membrane electrolysis is a bath maintenance technology that lowers or maintains the concentration of metallic impurities in cleaning solutions. This technology is also applicable to other metal-bearing solutions (e.g., electroplating, anodizing, and stripping solutions). This technology uses an ion-exchange membrane(s) and an electrical potential applied across the membrane(s). The membrane is ion-permeable and selective, permitting ions of a given electrical charge to pass through. Cation membranes allow only cations (e.g., copper, nickel, aluminum) to pass from one electrolyte to another, while anion membranes allow only anions (e.g., sulfates, chromates, chlorides, cyanide) to pass through. Bath maintenance units can be configured with cation or anion membranes, or both.

A typical application of membrane electrolysis is maintenance of an acid cleaning solution. The cleaning solution is placed in an anode compartment that is separated from a second electrolyte by a cation membrane. The solution in the cathode compartment (i.e., catholyte) is typically a dilute acidic or alkaline solution. When an electrical potential is applied, the dissolved metals in the cleaning solution migrate through the cation membrane into the catholyte. The catholyte is periodically discarded when it becomes saturated with metals.

D.4.3 Condition of the Surfaces Being Cleaned

The condition of the parts being cleaned varies widely, both in terms of the types and quantities of contaminants present and the quantity of oil. For example, some parts may have been wiped clean and have only a light deposit of metal-working fluids, while other parts may be heavily coated. Since metal-working fluids (oils) present on the parts are removed during the cleaning process (aqueous degreasing), the rate of oil that is entering into the cleaning solution per square foot of part cleaned will vary. The type of oil entering the cleaning solution will also affect the cleaning fluid's life-span.

D.4.4 Cleaning Requirements

Some processes, such as electroplating, require a high degree of cleanliness while others, such as phosphate conversion coating, may have less stringent requirements. The cleaning requirements will therefore vary within a facility, as well as from facility to facility, as will the type of cleaning process selected.

Some cleaning processes are more amenable to pollution prevention practices than others, based on the purpose of the cleaning process. For example, many electroplating processes require etching of the part's surface to enhance adhesion of the electroplated metal deposit. Surface etching introduces dissolved metal into the cleaning solution and will reduce its life-span.

D.4.5 Type of Cleaning Process and Equipment

The life-span of cleaning solutions depends on the type of cleaning process (i.e., process chemistry and cleaning equipment). Numerous factors affect the selection of a cleaning process, including: type and characteristics of contaminants to be removed; type and condition of base metal; size and configuration of parts; degree of cleanliness required; processing capabilities at the site; subsequent operations to be performed; and financial considerations.

The factors that most affect the selection of process chemistry and equipment are the type of contaminants present on the parts, type of base metal, and the subsequent finishing operation, which in turn dictate the cleaning requirements. Contaminants present on parts can include both organic and inorganic contaminants. Examples of organic contaminants are machining fluids, miscellaneous oils, waxes, and buffing compounds, which are typically removed by solvents, detergents, and alkaline solutions. Examples of inorganic contaminants are scale, smut, and grinding residue, which are typically removed by acidic solutions. Various methods are used to apply the cleaning solution. For example, solutions can be applied by spraying or immersing, and can be applied electrolytically (including both anodic and cathodic cleaning). Application method is primarily based on the concentration and condition of the contaminant and the configuration of the parts.

The base material of the parts is also a consideration in selecting a cleaning process. Some base materials are chemically or physically altered by certain cleaning steps because of oxidation, etching, activation, and hydrogen embrittlement. Such changes may be either desirable or damaging. The base material is also important in considering the operating conditions of the cleaning process (e.g., concentration, temperature, current). Further, the base material contaminates the cleaning solution (e.g., etching during acid treatment) and therefore affects the life span of the solution.

D.5 References

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Appendix E

MODIFIED DELTA-LOGNORMAL DISTRIBUTION

Appendix E

MODIFIED DELTA-LOGNORMAL DISTRIBUTION

This appendix describes the use of the modified delta-lognormal distribution to model treated effluent data and the estimation of the episode long-term averages and variability factors used to calculate the limitations and standards.¹ This appendix describes the statistical methodology that was used to obtain the results presented in Section 10.0.

The modified delta-lognormal distribution is a generalization of the familiar two parameter lognormal distribution. This generalized model can be used to model data sets that are a mixture of lognormally distributed values and values that are censored and/or assigned a constant value such as zero or a sample-specific detection limit. When only measured (i.e., noncensored) values are present in the data, such as all the data sets used to determine the limitations, the modified delta-lognormal distribution is equivalent to the familiar two parameter lognormal distribution. Researchers have concluded that the lognormal distribution is often useful for environmental data.^{2,3} Furthermore, EPA has found that the lognormal consistently provides a reasonably good fit to observed effluent data distributions.⁴ In this appendix, EPA has described the full model, that is, the modified delta-lognormal distribution, because it was used to calculate some of the loadings used in other analyses supporting this rule. This model has been used to develop effluent limitations for currently regulated industries including the Iron and Steel industry and the Centralized Waste Treatment industry.

E.1 Basic Overview of the Modified Delta-Lognormal Distribution

EPA selected the modified delta-lognormal distribution to model pollutant effluent concentrations from the MP&M industry in developing the long-term averages and variability factors. A typical effluent data set from a sampling episode or self-monitoring episode (see Section 3.0 for a discussion of the data associated with these episodes) consists of a mixture of measured (detected) and nondetected values. The modified delta-lognormal distribution is appropriate for such data sets because it models the data as a mixture of measurements that follow a lognormal distribution and nondetect measurements that occur with a certain probability. The model also allows for the possibility that nondetect measurements occur at multiple sample-specific detection limits. Because the data appeared

¹In the remainder of this appendix, references to 'limitations' includes 'standards.'

²e.g., see Richard O. Gilbert, Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold, New York, 1987.

³W.J. Owen and T.A. DeRouen, "Estimation of the Mean for Lognormal Data Containing Zeroes and Left-Censored Values, with Applications to the Measurement of Worker Exposure to Air Contaminants," *Biometrics* 36:707-719, 1980.

⁴See H.D. Kahn and M.B. Rubin, "Use of Statistical Methods in Industrial Water Pollution Control Regulations in the United States," *Environmental Monitoring and Assessment*, **12**: 129-148, 1989.

to fit the modified delta-lognormal model reasonably well, EPA has determined that this model is appropriate for these data.

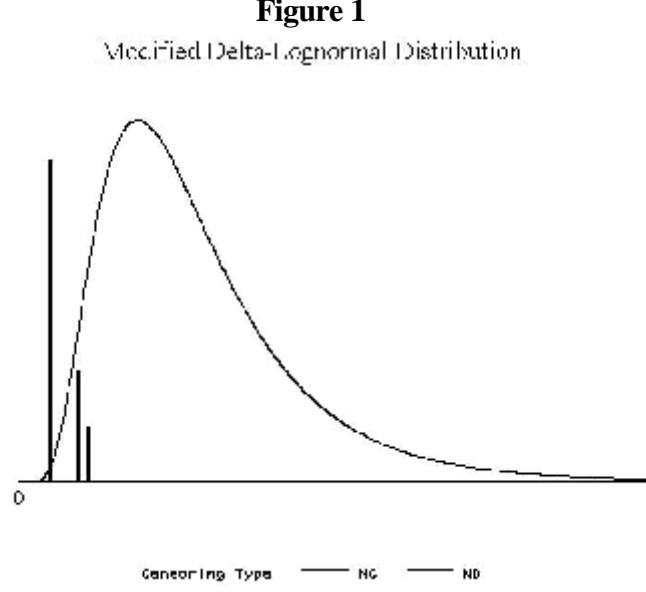
The modified delta-lognormal distribution is a modification of the 'delta distribution' originally developed by Aitchison and Brown.⁵ While this distribution was originally developed to model economic data, other researchers have shown the application to environmental data.⁶ The resulting mixed distributional model, which combines a continuous density portion with a discrete-valued spike at zero, is also known as the delta-lognormal distribution. The delta in the name refers to the proportion of the overall distribution contained in the discrete distributional spike at zero; that is, the proportion of zero amounts. The remaining nonzero, noncensored (NC) amounts are grouped together and fit to a lognormal distribution.

EPA modified this delta-lognormal distribution to incorporate multiple detection limits. In the modification of the delta portion, the single spike located at zero is replaced by a discrete distribution made up of multiple spikes. Each spike in this modification is associated with a distinct sample-specific detection limit associated with nondetected (ND) measurements in the database.⁷ A lognormal density is used to represent the set of measured values. This modification of the delta-lognormal distribution is illustrated in Figure 1.

⁵Aitchison, J. and Brown, J.A.C. (1963) The Lognormal Distribution. Cambridge University Press, pages 87-99.

⁶Owen, W.J. and T.A. DeRouen. 1980. "Estimation of the Mean for Lognormal Data Containing Zeroes and Left-Censored Values, with Applications to the Measurement of Worker Exposure to Air Contaminants." *Biometrics*, 36:707-719.

⁷Previously, EPA had modified the delta-lognormal model to account for nondetected measurements by placing the distributional "spike" at a single positive value, usually equal to the nominal quantitation limit, rather than at zero. For further details, see Kahn and Rubin, 1989. This adaptation was used in developing limitations and standards for the organic chemicals, plastics, and synthetic fibers (OCPSF) and pesticides manufacturing rulemakings. EPA has used the current modification in several, more recent, rulemakings.



The following two subsections describe the delta and lognormal portions of the modified delta-lognormal distribution in further detail.

E.2 Continuous and Discrete Portions of the Modified Delta-Lognormal Distribution

The discrete portion of the modified delta-lognormal distribution models the nondetected values corresponding to the k reported sample-specific detection limits. In the model, $*$ represents the proportion of nondetected values in the dataset and is the sum of smaller fractions, $*_i$, each representing the proportion of nondetected values associated with each distinct detection limit value. By letting D_i equal the value of the i^{th} smallest distinct detection limit in the data set and the random variable X_D represents a randomly chosen nondetected measurement, the cumulative distribution function of the discrete portion of the modified delta-lognormal model can be mathematically expressed as:

$$\Pr(X_D \leq c) = \frac{1}{d} \sum_{i: D_i \leq c} d_i \quad 0 < c \quad (\text{E-1})$$

The mean and variance of this discrete distribution can be calculated using the following formulas:

$$E(X_D) = \frac{1}{d} \sum_{i=1}^k d_i D_i \quad (\text{E-2})$$

$$\text{Var}(X_D) = \frac{1}{d} \sum_{i=1}^k d_i (D_i - E(X_D))^2 \quad (\text{E-3})$$

The continuous, lognormal portion of the modified delta-lognormal distribution was used to model the detected measurements from the MP&M industry database. The cumulative probability distribution of the continuous portion of the modified delta-lognormal distribution can be mathematically expressed as:

$$\Pr[X_C \leq c] = \Phi \left[\frac{\ln(c) - m}{s} \right] \quad (\text{E-4})$$

where the random variable X_C represents a randomly chosen detected measurement, M is the standard normal distribution, and m and s are parameters of the distribution.

The expected value, $E(X_C)$, and the variance, $\text{Var}(X_C)$, of the lognormal distribution can be calculated as:

$$E(X_C) = \exp \left(m + \frac{s^2}{2} \right) \quad (\text{E-5})$$

$$\text{Var}(X_C) = [E(X_C)]^2 \left(\exp(s^2) - 1 \right) \quad (\text{E-6})$$

E.3 Combining the Continuous and Discrete Portions

The continuous portion of the modified delta-lognormal distribution is combined with the discrete portion to model data sets that contain a mixture of nondetected and detected measurements. It is possible to fit a wide variety of observed effluent data sets to the modified delta-lognormal distribution. Multiple detection limits for nondetect measurements are incorporated, as are measured ("detected") values. The same basic framework can be used even if there are no nondetected values in the data set (in this case, it is the same as the lognormal distribution). Thus, the modified delta-lognormal distribution offers a large degree of flexibility in modeling effluent data.

The modified delta-lognormal random variable U can be expressed as a combination of three other independent variables, that is,

$$U = I_u X_D + (1 - I_u) X_C \quad (\text{E-7})$$

where X_D represents a random nondetect from the discrete portion of the distribution, X_C represents a random detected measurement from the continuous lognormal portion, and I_u is an indicator variable signaling whether any particular random measurement, u , is nondetected or noncensored (that is, $I_u=1$ if u is nondetected; $I_u=0$ if u is noncensored). Using a weighted sum, the cumulative distribution function from the discrete portion of the distribution (equation 1) can be combined with the function from the

continuous portion (equation 4) to obtain the overall cumulative probability distribution of the modified delta-lognormal distribution as follows,

$$\Pr(U \leq c) = \sum_{i: D_i \leq c} \mathbf{d}_i + (1 - \mathbf{d}) \Phi \left[\frac{\ln(c) - \mathbf{m}}{\mathbf{s}} \right] \quad (\text{E-8})$$

where D_i is the value of the i^{th} sample-specific detection limit.

The expected value of the random variable U can be derived as a weighted sum of the expected values of the discrete and continuous portions of the distribution (equations 2 and 5, respectively) as follows

$$E(U) = \mathbf{d} E(X_D) + (1 - \mathbf{d}) E(X_C) \quad (\text{E-9})$$

In a similar manner, the expected value of the random variable squared can be written as a weighted sum of the expected values of the squares of the discrete and continuous portions of the distribution as follows

$$E(U^2) = \mathbf{d} E(X_D^2) + (1 - \mathbf{d}) E(X_C^2) \quad (\text{E-10})$$

Although written in terms of U , the following relationship holds for all random variables, U , X_D , and X_C .

$$E(U^2) = \text{Var}(U) + [E(U)]^2 \quad (\text{E-11})$$

So using equation 11 to solve for $\text{Var}(U)$, and applying the relationships in equations 9 and 10, the variance of U can be obtained as

$$\text{Var}(U) = \mathbf{d} \left(\text{Var}(X_D) + [E(X_D)]^2 \right) + (1 - \mathbf{d}) \left(\text{Var}(X_C) + [E(X_C)]^2 \right) - [E(U)]^2 \quad (\text{E-12})$$

E.4 Episode-specific Estimates Under the Modified Delta-Lognormal Distribution

In order to use the modified delta-lognormal model to calculate the limitations, the parameters of the distribution are estimated from the data. These estimates are then used to calculate the limitations.

The parameters $\hat{\mathbf{d}}_i$ and $\hat{\mathbf{d}}$ are estimated from the data using the following formulas:

$$\begin{aligned}\hat{\mathbf{d}}_i &= \frac{1}{n} \sum_{j=1}^{n_d} I(d_j = D_i) \\ \hat{\mathbf{d}} &= \frac{n_d}{n}\end{aligned}\tag{E-13}$$

where n_d is the number of nondetected measurements, $d_j, j = 1$ to n_d , are the detection limits for the nondetected measurements, n is the number of measurements (both detected and nondetected) and $I(\dots)$ is an indicator function equal to one if the expression within the parentheses is true and zero otherwise. The "hat" over the parameters indicates that they are estimated from the data. When all of the data are noncensored, $\hat{\mathbf{d}}$ is equal to zero and the modified delta-lognormal distribution is equivalent to the lognormal distribution.

The expected value and the variance of the delta portion of the modified delta-lognormal distribution can be calculated from the data as:

$$\hat{E}(X_D) = \frac{1}{\hat{\mathbf{d}}} \sum_{i=1}^k \hat{\mathbf{d}}_i D_i \tag{E-14}$$

$$\hat{Var}(X_D) = \frac{1}{\hat{\mathbf{d}}} \sum_{i=1}^k \hat{\mathbf{d}}_i (D_i - \hat{E}(X_D))^2 \tag{E-15}$$

The parameters of the continuous portion of the modified delta-lognormal distribution, $\hat{\mathbf{m}}$ and $\hat{\mathbf{s}}^2$, are estimated by

$$\begin{aligned}\hat{\mathbf{m}} &= \sum_{i=1}^{n_c} \frac{\ln(x_i)}{n_c} \\ \hat{\mathbf{s}}^2 &= \sum_{i=1}^{n_c} \frac{(\ln(x_i) - \hat{\mathbf{m}})^2}{n_c - 1}\end{aligned}\tag{E-16}$$

where x_i is the i^{th} detected measurement value and n_c is the number of detected measurements. Note that $n = n_d + n_c$.

The expected value and the variance of the lognormal portion of the modified delta-lognormal distribution can be calculated from the data as:

$$\hat{E}(X_C) = \exp\left(\hat{\mathbf{m}} + \frac{\hat{\mathbf{s}}^2}{2}\right) \tag{E-17}$$

$$\hat{Var}(X_C) = \left[\hat{E}(X_C) \right]^2 \left(\exp(\hat{S}^2) - 1 \right) \quad (\text{E-18})$$

Finally, the expected value and variance of the modified delta-lognormal distribution can be estimated using the following formulas:

$$\hat{E}(U) = \hat{d} \hat{E}(X_D) + (1 - \hat{d}) \hat{E}(X_C) \quad (\text{E-19})$$

$$\hat{Var}(U) = \hat{d} \left(\hat{Var}(X_D) + \left[\hat{E}(X_D) \right]^2 \right) + (1 - \hat{d}) \left(\hat{Var}(X_C) + \left[\hat{E}(X_C) \right]^2 \right) - \left[\hat{E}(U) \right]^2 \quad (\text{E-20})$$

Equations 17 through 20 are particularly important in the estimation of episode long-term averages and variability factors as described in the following sections. These sections are preceded by a section that identifies the episode data set requirements.

Example:

Consider a facility that has 10 samples with the following concentrations:

| Sample number | Measurement Type | Concentration (mg/L) |
|---------------|------------------|----------------------|
| 1 | ND | 10 |
| 2 | ND | 15 |
| 3 | ND | 15 |
| 4 | ND | 20 |
| 5 | NC | 25 |
| 6 | NC | 25 |
| 7 | NC | 30 |
| 8 | NC | 35 |
| 9 | NC | 35 |
| 10 | NC | 40 |

The ND components of the variance equation are:

$$D_1 = 10, \hat{d}_1 = 1/10$$

$$D_2 = 15, \hat{d}_2 = 1/5$$

$$D_3 = 20, \hat{d}_3 = 1/10.$$

Since $\hat{\mathbf{d}} = 2/5$, the expected value and the variance of the discrete portion of the modified delta-lognormal distribution are

$$\hat{E}(X_D) = \frac{1}{2/5} \left(\frac{1}{10} \times 10 + \frac{1}{5} \times 15 + \frac{1}{10} \times 20 \right) = 15,$$

$$\hat{Var}(X_D) = \frac{1}{2/5} \left(\frac{1}{10} \times (10-15)^2 + \frac{1}{5} \times (15-15)^2 + \frac{1}{10} \times (20-15)^2 \right) = 12.5.$$

The mean and variance of the log NC values are calculated as follows:

$$\hat{\mu} = \frac{\sum_{i=1}^{n_c} \ln(x_i)}{n_c} = \frac{(2 \times \ln(25) + \ln(30) + 2 \times \ln(35) + \ln(40))}{6} = 3.44$$

$$\hat{s}^2 = \frac{\sum_{i=1}^{n_c} (\ln(x_i) - \hat{\mu})^2}{n_c - 1} = \frac{(2 \times (\ln(25) - 3.44)^2) + (\ln(30) - 3.44)^2 + (2 \times (\ln(35) - 3.44)^2) + (\ln(40) - 3.44)^2}{5} = 0.0376$$

Then, the expected value and the variance of the lognormal portion of the modified delta-lognormal distribution are

$$\hat{E}(X_C) = \exp \left(3.44 + \frac{0.0376}{2} \right) = 31.779$$

$$\hat{Var}(X_C) = [31.779]^2 (\exp(0.0376) - 1) = 38.695.$$

The expected value and variance of the modified delta-lognormal distribution are

$$\hat{E}(U) = \frac{2}{5} \times 15 + \left(1 - \frac{2}{5} \right) \times 31.779 = 25.067$$

$$\hat{Var}(U) = \frac{2}{5} \times (12.5 + 15^2) + \left(1 - \frac{2}{5} \right) \times (38.695 + 31.779^2) - 25.067^2 = 95.781.$$

E.4.1 Episode Data Set Requirements

Estimates of the necessary parameters for the lognormal portion of the distribution can be calculated with as few as two distinct detected values in a data set. (In order to calculate the variance of the modified delta-lognormal distribution, two distinct detected values are the minimum number that can be used and still obtain an estimate of the variance for the distribution.)

If an episode data set for a pollutant contained three or more observations with two or more distinct detected concentration values, then EPA used the modified delta-lognormal distribution to calculate long-term averages and variability factors. If the episode data set for a pollutant did not meet these requirements, EPA used an arithmetic average to calculate the episode long-term average and excluded the dataset from the variability factor calculations (because the variability could not be calculated).

In statistical terms, each measurement was assumed to be independently and identically distributed from the other measurements of that pollutant in the episode data set.

The next two sections apply the modified delta-lognormal distribution to the data for estimating episode long-term averages and variability factors for the MP&M industry.

E.4.2 Estimation of Episode Long-Term Averages

If an episode dataset for a pollutant meets the requirements described in the last section, then EPA calculated the long-term average using equation 19. Otherwise, EPA calculated the long-term average as the arithmetic average of the daily values where the sample-specific detection limit was used for each nondetected measurement.

E.4.3 Estimation of Episode Daily Variability Factors

For each episode, EPA estimated the daily variability factors by fitting a modified delta-lognormal distribution to the daily measurements for each pollutant. The episode daily variability factor is a function of the expected value, and the 99th percentile of the modified delta-lognormal distribution fit to the daily concentration values of the pollutant in the wastewater from the episode. The expected value, was estimated using equation 19 (the expected value is the same as the episode long-term average).

The 99th percentile of the modified delta-lognormal distribution fit to each data set was estimated by using an iterative approach. First, the pollutant-specific detection limits were ordered from smallest to largest. Next, the cumulative distribution function, p , for each detection limit was computed. The general form, for a given value c , was:

$$p = \sum_{i:D_i \leq c} \hat{d}_i + (1 - \hat{d}) \Phi \left[\frac{\ln(c) - \hat{m}}{\hat{s}} \right] \quad (\text{E-21})$$

where M is the standard normal cumulative distribution function. Next, the interval containing the 99th percentile was identified. Finally, the 99th percentile of the modified delta-lognormal distribution was calculated. The following steps were completed to compute the estimated 99th percentile of each data subset:

- Step 1 Using equation 21, k values of p at $c=D_m$, $m=1, \dots, k$ were computed and labeled p_m .
- Step 2 The smallest value of m ($m=1, \dots, k$), such that $p_m \leq 0.99$, was determined and labeled as p_j . If no such m existed, steps 3 and 4 were skipped and step 5 was computed instead.
- Step 3 Computed $p^* = p_j - \hat{d}_j$.
- Step 4 If $p^* < 0.99$, then $\hat{P}_{99} = D_j$
 else if $p^* \geq 0.99$, then

$$\hat{P}_{99} = \exp \left(\hat{m} + \hat{s} \Phi^{-1} \left[\frac{0.99 - \sum_{i=1}^{j-1} \hat{d}_i}{1 - \hat{d}} \right] \right) \quad (\text{E-22})$$

where M^{-1} is the inverse normal distribution function.

- Step 5 If no such m exists such that $p_m > 0.99$ ($m=1, \dots, k$), then

$$\hat{P}_{99} = \exp \left(\hat{m} + \hat{s} \Phi^{-1} \left[\frac{0.99 - \hat{d}}{1 - \hat{d}} \right] \right) \quad (\text{E-23})$$

The episode daily variability factor, VF1, was then calculated as:

$$VF1 = \frac{\hat{P}_{99}}{\hat{E}(U)} \quad (\text{E-24})$$

Example:€

Since no such m exists such that $p_m > 0.99$ ($m=1, \dots, k$), €

$$\hat{P}_{99} = \exp\left(3.44 + 0.194 \times \Phi^{-1}\left[\frac{0.99 - 0.4}{1 - 0.4}\right]\right) = 47.126.$$

The episode daily variability factor, VF1, was then calculated as:

$$VF1 = \frac{47.126}{25.067} = 1.880.$$

To identify situations producing unexpected results, EPA reviewed all of the variability factors. EPA used several criteria to determine if the episode daily variability factors should be included in calculating the option variability factors. One criteria that EPA used was that the daily variability factors should be greater than 1.0. A variability factor less than 1.0 would result in an unexpected result where the estimated 99th percentile would be less than the long-term average. This would be an indication that the estimate of \hat{S} (the log standard deviation) was unstable. A second criteria was that not all of the sample-specific detection limits could exceed the values of the noncensored values. All the episode variability factors used for the limitations and standards met these criteria.

E.5 References

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